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Report of the Chief of the Bureau of Agricultural and Industrial Chemistry

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UNITED STATES DEPARTMENT OF AGRICULTURE
Agricultural Research Administration

Report of the Chief of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, 1953

United States Department of Agriculture,
Washington, D. C., September 1, 1953.

Dr. B. T. Shaw,
Agricultural Research Administrator.

Dear Dr. Shaw: I present herewith the report of the Bureau of Agricultural and Industrial Chemistry for the fiscal year ended June 30, 1953.

Sincerely,

G. E. Hilbert,
Chief.

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INTRODUCTION

The research program of the Bureau of Agricultural and Industrial Chemistry has a threefold objective; namely, (1) to provide more income for the farmer from the crops which he grows, (2) to assist industry in converting agricultural raw materials into new and improved products, and (3) to devise means for making these products available to the consumer at reasonable costs.

This type of research is broadly called utilization research and can roughly be divided into three phases. One phase is concerned with the conversion to stable form of the produce from the farms shortly after it is harvested so that it can be stored without serious loss or damage and made available in adequate quantities for use when needed. A second phase is designed to improve the processing of agricultural commodities by streamlining processes, developing new and improved equipment, and reducing loss and wastage of material to a minimum. A third phase is concerned with the creation of new and more valuable materials from agricultural products not now finding their most advantageous market.

The Bureau's research is conducted at 4 large regional research laboratories and 10 smaller field laboratories. Because of space limitations, it is impossible to describe all the lines of work that have engaged the attention of the Bureau's research personnel during the fiscal year 1953. The items selected for inclusion in this report are grouped under 5 main headings, 4 of which indicate the principal outlets in which the agricultural products are utilized; namely, (1) foods and feeds, (2) fibers and fiber products, (3) medicinals, and (4) industrial products. The fifth group includes basic and pioneering investigations, which have played and must continue to play an important role in the efficient utilization of farm crops.

The number of items in the fifth group is somewhat over 25 percent of the total number included in the report for 1953. This is consistent with the statement made in the Bureau's report for 1952 that basic research is a necessary prerequisite to the development of new products from agricultural commodities that will be acceptable for industrial and consumer use. The following examples from the present report show some of the accomplishments resulting from basic investigations.

Practical results of basic investigations.—The Bureau's Northern Regional Research Laboratory has devoted attention for many years to the collection and identification of a large number of organisms capable of converting agricultural products into potentially useful chemical compounds. During World War II, this culture collection furnished the organism—originally obtained from a rotten cantaloup—upon which was based the commercial production of penicillin. More recently, this same culture collection was searched for an organism which could be used for the large-scale production of

dextran, a compound found to be useful as a substitute or extender for blood plasma. A dextran-producing organism—originally isolated from a bottle of spoiled root beer and designated as NRRL B–512—was found to be so satisfactory for this purpose that it has now been adopted as the standard strain for the commercial production of clinical dextran in the United States. During the past year, the Northern Laboratory has assisted dextran producers by developing improved processes for the more economical production of clinical dextran and improved analytical and physical methods for controlling the quality of the dextran produced.

A basic study of the composition of casein produced from skim milk revealed that it could be separated into three protein components, called alpha-, beta-, and gamma-casein. A method for accomplishing this separation was developed and the three types of casein were produced in sufficient quantities for practical evaluation. Beta-casein was found to be superior to the other two caseins for the production of coatings and fibers.

Information has been obtained concerning some of the minor constituents of alfalfa. Compounds known as saponins have been found to be present in some varieties in amounts up to 1 percent of the dry weight of the alfalfa. These compounds have been shown to inhibit the growth of chicks when incorporated in their feed and preliminary tests indicate that they can produce bloating in ruminants. Hence, efforts will be made cooperatively to develop varieties of alfalfa in which the saponin content is at a minimum.

New light has been shed on the causes of the enzymatic browning that takes place in many kinds of fruits when their cut surfaces are exposed. Small amounts of two substances which belong to the family of tannins have been shown to be present in peaches, apricots, and prunes. These substances have the property of turning brown through a reaction with the oxygen in air stimulated by an enzyme present in the fruit. This knowledge will be helpful in developing means for the prevention of browning in fruits.

Basic information has been obtained on the structure of the corn kernel, including the hull, endosperm, and germ. This is proving to be of great value to corn handlers and processors. Numerous requests have been received from industrial concerns for reprints of the published articles which describe the structure of the kernel in some detail.

Similar information on the structure of the cotton fiber is expected to be helpful to the cotton-processing industry. Continued studies of the primary wall of the fiber are furnishing valuable assistance in evaluating the effects of various chemical finishing treatments upon the fibers which go to make up the yarn and fabric structure.

Investigations of the flameproofing of cotton fabrics have led to development of a theory which postulates that as a result of the flameproofing reaction, the decomposition of the cotton cellulose by fire is changed from a reaction giving volatile flammable products to one giving mainly water and a highly carbonaceous char. This theory serves as a guide to the selection of resins or other compounds which would be expected to be most effective for flameproofing purposes.

Conversion of fruits and vegetables to stable form.—This report contains many examples of the conversion of perishable agricultural crops into stable forms which can be stored without lowering their

value for food or feed purposes. A few examples of this type of research are cited herein.

Studies at the Eastern Regional Research Laboratory have resulted in the development of fat-fried products from carrots, beets, parsnips, lima beans, and peas. These products, which are analogous to potato chips, have acceptable flavor and texture characteristics.

Manufacturers of frozen orange concentrate have benefited from studies in the Western Region which show that stability of the concentrate during transportation and storage can be noticeably improved, without loss of flavor, by brief application of direct steam injection heating to inactivate enzymes. Other studies during the past year have resulted in the development of a pure orange powder which remains stable after long periods of storage, even at elevated temperatures, and can be reconstituted almost instantaneously into orange juice. Furthermore, it has been demonstrated that the storage life of packaged dehydrated fruits and vegetables can be extended severalfold by including a small sack of a desiccant, such as calcium oxide, in each package.

Studies in the Southern Region have resulted in development of an unsweetened frozen lime-juice concentrate, 1 pint of which is capable of producing about 4½ gallons of limeade. The production of this limeade base not only provides an additional outlet for limes which mature during the summer months but also utilizes concentration equipment which operates on oranges and grapefruit in other seasons of the year.

Improvements in processing agricultural commodities.—The Eastern Regional Research Laboratory has shown that the so-called "leach pressing" of apples increases the yield of full-flavored apple juice concentrate, and that an oil-firing evaporator for maple sap produces sirup of more uniform quality and reduces the processing cost.

Improved procedures for the milling of rice which should result in less breakage of rice grains and a higher yield of whole grain, have been developed by investigations at the pilot-plant rice mill of the University of Arkansas under a contract supervised by the Southern Laboratory. In studies at the laboratory, a determination has been made of the processing conditions which will result in conversion of peanuts into peanut butter of optimum quality. The new filtration-extraction process for cottonseed, reported by the Southern Laboratory last year, is now being adapted for use with other oilseeds, such as sesame, peanuts, and milo germ.

Cotton processors have been furnished with a new roving twist formula developed in the textile mill at the Southern Laboratory. A nomograph, based on the formula, enables rapid determination of the optimum twist required for a wide range of carded rovings when the staple length and fineness of the cotton fibers are known.

Industrial products from farm crops.—Chemical treatment of cotton fabrics by the process known as partial acetylation is now being practiced on a commercial scale. This process—developed at the Southern Laboratory—improves the heat- and rot-resistance of cotton while retaining all its natural good qualities. The treated cloth is especially adapted for use in pads and covers for laundry presses and home ironing boards because of its superior resistance to deterioration by heat.

A new flameproofing treatment for cotton is being evaluated on a semi-commercial scale. The treatment involves use of a chemical (called THPC) and a resin which impart to cotton cloth both flameproofness and wrinkle-resistance. The treated cloth retains its flameproofness through many launderings and it is particularly suitable for use in clothing, draperies, and curtains.

The Eastern Laboratory has shown that animal fats, suitably processed, are fully as satisfactory as imported palm oil for use in the hot-dip tinning of steel sheets for can manufacture. Reaction of the fats with organic peracids converts them into products (called epoxidized fats) which have the valuable property of plasticizing and stabilizing vinyl chloride plastics so that their useful life is increased.

Work on agricultural residues at the Northern Laboratory has demonstrated that sugarcane bagasse can readily be separated into pith and fiber. Pulp made from the depithed fiber by the mechanochemical process was used for the production of corrugating and liner boards. These boards proved to be entirely satisfactory for manufacture of beverage shipping containers. This development demonstrated that the new process of pulping bagasse is ready for industrial application.

Publications and patents.—Further information on the Bureau's work is available in the official publications that appeared during the year. Bureau employees contributed 439 printed and processed publications. Most of them were research papers published in non-Government scientific and technical journals. Usually a limited number of reprints of such papers are bought for distribution to seriously interested individuals and firms as long as the supply lasts.

Information on newly developed processes and products is given in the specifications of the 67 patents granted to Bureau scientists.

More than 27,000 letters requesting information and publications were received by the Bureau during the year.

FOODS AND FEEDS

Fruits

Applesauce flavor improved by addition of essence and citric acid

Among the many processed apple products, applesauce ranks second to vinegar in volume of fruit utilized. Since the best grade of cull apples are used in sauce manufacture, return to the grower is approximately three times the value for vinegar-grade fruit on a unit volume basis. Advances in applesauce processing during the past 30 years have been confined to improvement in mechanical equipment and to limited studies on control of consistency and defects. Although the product has been well standardized with regard to uniformity of color and texture, there has been little improvement in the characteristically bland flavor.

Preliminary studies by the Bureau's Eastern Regional Research Laboratory in cooperation with an industrial concern indicate that applesauce flavor can be greatly improved by addition of small amounts of apple essence and citric acid. These additions impart a fresh, tart flavor which is superior to that of applesauce prepared from whole apples by the housewife. From the processor's standpoint it is

significant that results to date indicate that the essence recovered from peels and cores is superior to that obtained from either a dessert blend or a sauce blend of apples. Processors experienced in manufacturing and marketing apple products have expressed the belief that improvement in the flavor of applesauce would greatly expand the market for this commodity. Success in this study of additives would also provide a new outlet for apple essence, a product which has found commercial use in apple concentrate, juice, jelly, candy, and several nonapple products since its original development by this laboratory in 1944.

Leach-pressing of apples increases yield of full-flavor concentrate and reduces cost

An improvement in the manufacture of full-flavor pure applejuice concentrate has been developed on a pilot-plant scale at the Eastern Regional Research Laboratory. This improvement, "leach pressing," gives an increase of 12 to 18 percent in yield of concentrate per ton of apples. The ground apples are pressed, the cakes of pomace disintegrated, water of approximately equal weight added, and the moistened pomace again pressed. The added water is removed when the juice is evaporated to make the concentrate.

Previous attempts to repress pomace, with or without water, have resulted in fresh flavor loss, introduced a so-called "oxidized" flavor, and caused slight fermentation. By adding water promptly to the pomace, and carrying out all operations between the pressings as quickly as possible, these deteriorations are avoided. Concentrate containing the second pressed juice, when diluted to drinking strength, yielded a high-grade applejuice, equal in quality to the single-pressed product. Storage tests of the concentrate at 35° F. are in progress, but results are not yet available.

The United States Standards for Grades of Canned Apple Juice of single strength exclude juice of a second pressing. No United States standards exist for applejuice concentrate.

Although the added water increases the cost of evaporation, this is more than offset by the increase in yield, with the result that net financial return is appreciably greater. Experimental runs were made using three different amounts of added water, viz, 75, 100, and 150 percent of the weight of the once-pressed pomace. For each of the three, a yield figure was obtained and a complete estimate made of the overall cost of producing concentrate, based on a season of 75 days, 16 hours a day, with apples at $20 per ton. The 100 percent water addition gave the lowest overall cost per can of concentrate. Under these conditions the cost was 0.9 cent per can less than with single pressing, and 16 percent more cans can be made from a given crop of apples without impairment of product quality.

Steam-injection heating stabilizes frozen orange concentrates

Manufacturers of frozen orange concentrate have little control over methods used in handling and distributing their product once it leaves their plant. Exposure of frozen concentrates to abnormal temperatures during handling, transportation, and storage may cause considerable loss of quality in these products before they reach the consumer. Loss of cloud, the initial change in frozen orange concentrates exposed to elevated temperatures, has become a problem and most processors now apply some type of heat treatment in the course of manufacture

to inactivate the enzymes responsible for this loss. The practice has developed so rapidly that there has been little opportunity to evaluate the process used, or to determine optimum conditions of heat treatment that will stabilize orange concentrates without materially altering the characteristic flavor.

Studies have been undertaken at the Bureau's Fruit and Vegetable Chemistry Laboratory in Pasadena, Calif., on the application of direct steam injection heating (a development described in the Bureau's reports for 1950 and 1952) in the rapid heat-processing of orange concentrates to obtain maximum stability with minimum flavor change. These studies have included investigations of the time-temperature effects of steam injection heating, and the interrelationships of time and temperature and product concentration at time of heating. The conditions studied included temperatures of 150°, 175°, and 200° F. for 1 and 20 second holding times, applied to juices of 12°, 27°, 43°, and 58° Brix concentration.

The results of these studies showed that the concentration of the product to which a particular heat treatment was applied was an important variable having a marked effect on inactivation of pectinesterase and degree of cloud stability obtained. In general, application of heat at any of the higher juice concentrations brought about a greater inactivation of pectinesterase, and a greater increase in cloud stability than was obtained when single strength juices were heated. However, the greater the juice concentration and the higher the temperature used, the greater the possibility of flavor damage. This would indicate that a relatively mild heat treatment applied to concentrated orange juice may achieve an acceptable cloud stability without flavor damage. Under these conditions the cost of the heating step is low.

Comparisons of data on cloud stability and on residual pectinesterase activity after concentrated juices had been steam heated, did not reveal such a direct relationship that cloud stabilization could be quantitatively predicted on the basis of pectinesterase inactivation. In general, however, cloud stability increased with increased destruction of this enzyme.

Under the conditions of these experiments the effect of temperature on cloud stability was greater than the effect of holding time. There was some indication that at certain "critical" temperatures, increased holding times may adversely affect cloud stability. When relatively mild temperatures were applied to concentrated juices for short holding times, the cloud stabilities obtained were similar to those obtained by application of higher temperatures to single strength juices. It was concluded that a high degree of cloud stability can be obtained using direct steam injection heating, without materially altering juice flavor.

Effect of temperature storage and time on quality of frozen fruit products

To maintain their high initial quality for extended periods, frozen fruit products should be kept at low temperatures. However, a completely satisfactory practical definition of this temperature requirement has not yet been formulated. Losses of quality, attributable to adverse temperature conditions sometimes encountered in storage or distribution of the frozen foods, have been of increasing concern

to the industry. Full consideration of remedial measures has, however, been hampered by lack of comprehensive information about the behavior of frozen foods under a wide range of conditions.

The necessary information about the behavior of several frozen fruits is being obtained at the Western Regional Research Laboratory, and more recently similar studies have been initiated on the leading frozen vegetables. The behavior of frozen orange juice concentrate is being studied at the Bureau's Fruit and Vegetable Chemistry Labroratory in Pasadena, Calif.

In the experiments large samples of commercially frozen products are exposed to constant and cyclic temperature patterns ranging from minus 20° to plus 40° F. over a period of up to 2 years. In other tests samples are subjected to patterns of temperature change similar to those that actually occur in storage and distribution. Samples withdrawn from time to time are evaluated for flavor, appearance, and texture by trained tasters in the laboratory and by cooperating quality-control and executive personnel from the industry. Numerous objective physical and chemical tests are also made, and some of the measurements thus obtained show good correlation with the subjective evaluations.

The work is intended to provide answers that will be applicable to the problems of frozen food processors throughout the country; consequently, each product is sampled in each of the major producing areas in the United States in each of several years, to bring out any variations in stability caused by seasonal differences. Detailed reports of the effects of the various temperature histories will be made only when adequately representative results have been obtained. Interim results from the unfinished study are, however, of interest.

The frozen fruits under investigation are strawberries, peaches, red raspberries, and red sour pitted cherries, all packed commercially in the retail size package. In the strawberries, the loss of ascorbic acid appears to be a sensitive indicator of quality loss. Browning and fading of color, which can be measured objectively, also show fairly good correlation with other quality changes. The most rapid change in peaches upon exposure to adverse conditions is browning of the slices. In both raspberries and sirup-packed red sour cherries, changes take place in the distribution of color between the fruit and the surrounding sirup at all temperatures above about 10° F. Under adverse conditions cherries also show serious browning.

In the samples of stored frozen orange juice concentrate, changes in flavor have taken place more slowly than loss of "cloud." Rate of damage to cloud stability increases rapidly as storage temperature rises, but is also appreciable in very long storage periods even at 0° F. The reactions which bring about cloud loss or flavor change are cumulative in their effects, so that two or more adverse temperature experiences may produce serious change even though the effect of any one of them would have been negligible.

Progress in development of stable orange powders

Much new information on factors affecting the storage stability of orange powder containing added corn sirup solids (announced in the Bureau's report for 1952) has been obtained. Of all factors studied, moisture content was found to affect stability most, particularly at elevated storage temperatures. Through use of improved in-package

desiccation procedures it was possible to attain the extremely low moisture content of 0.5 percent or less. Such material was still acceptable after 6 months of storage at 100° F., and a year of storage at room temperature produced no significant changes. Application of a recently developed procedure for "locking-in" the orange flavor was found to minimize oxidative changes in the flavor fraction during storage. Stability of orange powder when stored at elevated temperatures was markedly increased by use of a small amount of sulfur dioxide (200 parts per million on a dry-weight basis), which does not adversely affect juice flavor.

By slight modification of procedures used in preparing orange powder with added corn sirup solids, workers at the Western Regional Research Laboratory have more recently produced a pure orange powder. Like the earlier product, it is readily reconstituted into orange juice by the addition of water. Although tests of its stability during storage have started, the development is still too recent to permit any report of storage results. There are indications, however, that effective functioning of the in-package desiccant before the product is subjected to high-temperature storage is even more vital than it is for orange powder containing added corn sirup solids.

A number of other investigators have published accounts of the preparation of orange juice powder, and semicommercial quantities of it were produced by one firm during World War II. Lack of sufficiently comprehensive knowledge of factors affecting its stability during subsequent storage may have been responsible for failure of full commercial development to follow these earlier investigations.

For evaluation as a subsistence item in Army camps, the Quartermaster Corps is making a study of the Bureau's method for manufacturing orange juice powder containing added corn sirup solids.

Frozen strawberry juice concentrate developed

The storage and shipment of frozen strawberry juice, containing only 5 to 10 percent solids, involves handling much water that must be removed during jelly manufacture. A method which will provide a concentrated juice that retains volatile flavor constituents and color and assumes uniform quality, has been developed by workers at the Western Regional Research Laboratory.

This process, similar to that for making frozen applejuice concentrate, consists of recovering volatile flavor constituents from depectinized and clarified juice, vacuum concentration of the stripped juice, and returning the volatile flavor constiuents to the concentrate. Dilution of the concentrate with water gives a product comparable to single-strength juice in color, flavor, and clarity. The new research involved determination of suitable conditions for degradation of pectic substances in strawberry juice by pectic enzymes. Even single-strength juice tends to gel during storage, and concentration increases this tendency. Investigation of the degree of concentration attainable showed that depectinized and clarified strawberry juice can be concentrated to as high as 73° Brix (reduction to about one-twelfth of the original volume) without damage to flavor or color.

Commercial production of sevenfold concentrate (about 48° Brix) has been undertaken by one manufacturer. Volatile flavor constituents are recovered in a unit patterned after the essence recovery unit developed by the Bureau's Eastern Regional Research Laboratory, as

modified for steam injection by the Western Laboratory. Concentration is carried out in a natural-circulation, external-calandria type of vacuum evaporator.

Removal of thrips from harvested raspberries

Small insects known as thrips are sometimes found in great numbers on raspberries, and attempts to control these insects in the field by sprays and dusts have met with little success. The problem of devising a method for effectively removing the insects without damaging the fruit has been investigated at the Fruit and Vegetable Products Laboratory at Puyallup, Wash. Experiments were carried on in cooperation with the Oregon Agricultural Experiment Station.

To find a reliable method of removing thrips, such methods as vibrating dry riddles, shaker washers, whirlpool washers, air blowers, sprays, and vacuum-cleaner devices have been tried. None were dependable or entirely effective. Devices similar to these were tested at the Puyallup laboratory and found to be little more effective than ordinary washing methods.

At this same laboratory, a far more effective method was devised. The berries are immersed in a dilute solution of a wetting agent, removed from this solution by an endless belt and washed in clear water to remove insects and the residue of wetting agent. The efficiency of insect removal from heavily infested berries by this relatively simple means is about 4 or 5 times greater than by previous methods which left about half of the original total number of adult insects and larvae on the berries. The improved technique reduces this contamination to only 5 to 15 percent of the original count. Use of this new technique of cleaning berries requires careful selection of a wetting agent and close attention to the washing and rinsing procedure. The wetting agent used in the experimental work was a mixture of alkylaryl sulfonate and sodium sulfate. Effective final washing and rinsing reduced the amount of this agent remaining with the berries to a range of 0 to 20 parts per million. Acceptability of such residue from the standpoint of public health remains to be determined by health authorities.

Observations made during the 1952 experiments have revealed no deleterious effects on color, flavor, or texture of the processed berries after cleaning by this method. Additional research is required, however, and will be continued during the 1953 season.

Frozen limeade bases further improved

The Bureau's 1952 report described a new frozen limeade base that had advantages over the present commercial product. This limeade, developed by the United States Citrus Products Laboratory at Winter Haven, Fla., could be prepared as a sweetened eightfold concentrate or as an unsweetened sixteenfold concentrate. Investigations during the past year have further improved the quality of the sweetened concentrate and more than doubled the concentration of the unsweetened product. In addition to the eightfold and sixteenfold products, an unsweetened superconcentrate of thirty-fivefold can be prepared. The latter product is especially interesting to the Armed Forces where weight and space savings are of prime importance.

Taste tests have revealed consumer preference for limeades of about 11 percent soluble solids (mainly sugars) with solids-to-acid

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ratios of from 14:1 to 16:1, and a peel oil content of about 0.004 percent by volume. The "cutback" procedure (addition of fresh unpasteurized juice) of making concentrates is not practical for lime superconcentrates because the large dilution involved requires a high oil content in the concentrate. Addition of refined lime peel oils enhances the flavor markedly, but the resulting product still does not yield limeades of top flavor. When properly prepared purees are used in place of fresh single-strength juice to reinforce concentrate flavor, the limeades produced are equal to those from fresh juice. Lime puree is prepared by passing the cut fruit through a screw press. The resultant product contains about 0.40 percent peel oil.

Sweetened limeade concentrate is prepared by concentrating about 7.5 volumes of lime juice to 3 volumes, adding 1 volume of puree, sweetening to about 68 percent soluble solids, and freezing. Preparation of the limeade is very simple—7 volumes of water to 1 volume of concentrate.

Unsweetened thirty-fivefold limeade concentrate is prepared by concentrating about 12 volumes of fresh juice to 2 volumes, adding 1 volume of puree, and freezing. Limeade is prepared by adding about 4 pounds of sugar to 1 pint of concentrate and diluting to 4⅜ gallons.

Since most limes in Florida mature during the summer months when there is little activity in oranges and grapefruit, production of a limeade base could provide not only an additional outlet for limes but profitable utilization of concentration equipment during the slack season.

Methods of preparing natural-colored canned juice from Texas pink and red grapefruit investigated

Eighty percent of the citrus trees of the Lower Rio Grande Valley were destroyed by severe freezes in 1949–51, temporarily halting commercial canning. Citrus orchards are being replanted at the rate of more than 1.5 million trees per year, and by 1954 it is anticipated that canning of citrus juice on a limited scale will be resumed. Replantings have been almost entirely pink or red grapefruit trees because of the great demand for such fruit on the fresh market, and its high quality. In order to maintain the market advantage of colored fruit rigid standards of quality must be maintained, and at least 25 percent of the fruit produced will be culls or fruit suitable only for juice production. Commercial methods of canning juice from colored fruit have not yielded a satisfactory product, for the juice is "muddy" and brown in appearance.

The United States Fruit and Vegetable Products Laboratory at Wesloco, Tex., has made progress in developing methods of processing this juice to obtain a natural pink color. A study of the pigments from which the color of pink grapefruit is derived has shown that the coloration is almost entirely due to the water-insoluble pigments, lycopene and carotene. Carotene is yellow and lycopene pink or red. Variations in the amounts and ratio of these compounds determine the shade of the fruit. Pigmentation occurs entirely in the cell walls and tissue, not in the cell juice. Because of the insolubility of these pigments, it has not been possible to add color directly to the juice.

Since the color is in the pulp, normally removed when the juice is screened, methods were sought of adding this pulp to the juice in

such a form that it would stay dispersed. When screened pulp is mixed with a small amount of juice and passed through a colloid mill the pulp is so finely dispersed that it remains suspended. It was found that if this suspension is added back to the original juice and again run through a colloid mill, a stable suspension of pigmented pulp in juice is obtained. This "naturally colored" juice has been canned as single-strength juice, and also prepared as a frozen concentrate. Preliminary storage experiments and taste appraisal tests indicate that this juice retains its color and quality and does not develop the "muddy" tint characteristic of juice prepared from colored fruit by customary procedures.

Work is in progress on the effect of added pulp on the total solids and naringin (bitter component) content of canned juice. The effect of fruit maturity on lycopene-carotene content, and on the color and quality of pulp-fortified juice is also being studied. Indications are that there is a definite stage of development (barely mature) at which fruit should be processed if maximum color is sought.

Vegetables

New precooked, dehydrated vegetable products

Studies by the Bureau's Eastern Regional Research Laboratory have resulted in development of new precooked, dehydrated vegetable products which offer promise of a variety of military and civilian uses. These novel food items, analogous to potato chips, were prepared from carrots, beets, parsnips, lima beans, and peas, by deep fat frying. The resulting vegetable chips or particles have highly acceptable flavor and texture characteristics. Peas and lima beans. dehydrated by this method, have a unique nutlike flavor whereas the carrot, beet, and parsnip chips retained most of their flavor characteristics and were sweeter than potato chips. All of these products offer promise as snack items.

The dehydrated lima beans and peas were also crushed and compressed into bars which are of interest for military rations because of their high protein, carbohydrate, and oil content. In addition, these materials have potential use in dehydrated soup mixes. Since large sized, very mature peas are best suited for this type of dehydration, a new outlet may be provided for peas of grade 5 and over at processing plants.

It was demonstrated that the time and temperature of dehydration varies with each vegetable and that optimum conditions are influenced by such factors as variety, maturity, chip size, and shape. Attempts are being made to improve these experimental conditions in order to obtain vegetable chips of good color, characteristic flavor, and long shelf life. Samples prepared early in this investigation were considered to be completely acceptable and commercially promising by industrial representatives in attendance at the National Meeting of the Potato Chip Institute.

Effect of cellulosic material on tomato juice consistency

Both tomatoes and tomato juice contain about 94 percent water. The enormous increase in fluidity on juicing comes about through separation and breakage of tomato tissue cells. Juice consistency may be much different if the product is to be used as a beverage or

manufactured into another type of food, such as soup, catsup, or paste. This consistency can be controlled or modified best when the causative agents are known. One such agent is pectin derived from intercellular cement and dissolved in the serum or filterable part of the juice. Another is insoluble suspended material consisting of intact cells whose walls are largely cellulosic, cell fragments, and associated insoluble pectic substances. Experiments designed to test the importance of this second group in determining tomato juice consistency have been undertaken cooperatively at the Eastern Regional Laboratory and the New York Agricultural Experiment Station, at Geneva.

In these experiments tomatoes were dissected and juice extracted from the outer shell, core and inner partitions, seed cavity, and seed envelope. Serum from the seed envelope was highly viscous and contained a large proportion of dissolved pectin. Juice from the seed cavity was very thin, contained few cells and little pectin. Juices from the shell and core were about equal in content of pectin and cellular material, and in consistency. Juices were also prepared from whole tomatoes, with the natural pectin-degrading enzymes both active and inactive during maceration and extraction. The effects on consistency of vigorous mechanical treatment and of added pectin-degrading enzymes were noted. The amount and configuration of cellulose in the juices were followed microscopically and recorded in photomicrographs.

Data obtained indicate that cellulosic material is an extremely important factor in determining juice viscosity. Juices of high cellulose content are viscous, whereas those of low cellulose content always have low viscosity, irrespective of the presence or absence of pectin. Changing the cellulose configuration, as in a homogenizer, usually increases the consistency considerably. The contribution of serum to total juice consistency is almost invariably quite small. In juices of very high pectin content enzymatic destruction of the pectin greatly reduces consistency. Extent of the decrease depends partly on the configuration of the cellulose. The consistency of enzyme-treated, pectin-free juice may, however, be either restored to its original value or made to much exceed that value by mechanical treatment of residual cellulosic material. The enzyme acts not only on pectin in the serum but also on pectin permeating the cellulose walls, as is evidenced by the increased crystallinity and brittleness of the cellulose and by its decreased tackiness.

Experimentation will be continued, for it is believed that a fuller understanding of what takes place during the manufacture of tomato juice may enable the processor to exercise greater control over yield and characteristics of the final product. The study may profitably be extended to include other foods in which cellulose and pectin apparently exert a strong influence on consistency.

New process for drying potato granules to very low moisture content

Present types of primary driers cannot be effectively utilized for drying potato granules (mashed potato powder) to the low moisture level necessary for good storage stability. Drying the granules to such low moisture content in a single pass through a conventional drier results in serious heat damage; multiple passes, moreover, can cause serious mechanical damage to the product and waste of heat.

These difficulties are encountered even if the product is dried only to 7 percent moisture, as required by present military specifications; they would become more serious if an attempt were made to assure better storage stability at high temperatures by reducing the moisture content of the product much below this standard.

Although the airlift drier developed at the Western Regional Research Laboratory, described in the Bureau's report of last year, does an excellent job of drying the granules without causing significant mechanical damage, it is not capable of achieving the extremely low moisture content now sought. To meet this problem, workers at the laboratory have developed and tested on a pilot-plant scale a *fluidized bed drier* to be used as a *secondary stage* to supplement the airlift drier.

The continuous fluidized bed drier comprises an insulated rectangular chamber fitted with a porous refractory plate as a false bottom, a hot-air plenum chamber beneath the porous plate, a cool-air outlet, a product inlet, and a product outlet. As the hot air emerges from the upper surface of the porous plate it "fluidizes" or suspends the bed of granules above the plate so that they move about like a boiling liquid. The liquid-like properties of the fluidized granules make it possible to operate the drier continuously by simple means. Granules are fed into one end of the drier so that a layer of material is maintained in the chamber; further addition of granules causes an equal amount of material to overflow a dam at the outlet. The granules flow into, through, and out of the drier just as a liquid would flow through a rectangular tank of similar construction. The continuous and thorough mixing of the granules by air insures uniform drying of the material. In the fluidized bed drier, potato granules have been dried at practical rates to moisture contents as low as 3 percent without appreciable damage to the product.

In this new method for drying potato granules, most of the heat is transferred by conduction from the porous plate to the granules. Ordinarily, heat is transferred by convection from the gas stream to the fluidized solid, or from the solid to the gas stream. The new method is possible because individual potato granules are so small and light that an air velocity of only 7 to 10 feet per minute is required for fluidization. The low air consumption limits the amount of heat supplied per unit time to a low value. As a result, even though air enters the porous plate at a temperature of 400° F., the top of the plate in contact with the granules is cooled by conduction to a temperature of only 200° to 225° F. Thus, the ever-changing layer of granules adjacent to the plate is in contact with a comparatively cool surface, and the possibility of product scorching is minimized. Heat utilization is excellent.

The merits of this new drying process have been established, and equipment design work is now in progress so that the process can be adapted to commercial production. Possible broader application of the principle of fluidized bed drying to other finely divided food products is now under consideration.

Dehydrofrozen pimiento

The potential value of dehydrofreezing, a new process developed by the Western Regional Laboratory for preserving various fruits and vegetables, was described in the Bureau's annual reports for 1946 and 1947. In this process, raw materials are carried through the first

phase of dehydration, then frozen, and subsequently held in frozen storage until used. The evident advantages of dehydrofreezing—fresh flavor retention, product stability, and economics of handling and storage as a consequence of reduced weight and volume—prompted an inquiry from a dairy food manufacturer in regard to the possible use of dehydrofrozen pimientos in the manufacture of cheese and other dairy food products.

In response to this inquiry, dehydrofrozen pimientos were prepared on the basis of knowledge and prior experience gained from similar processing of peas, carrots, lima beans, corn, etc. Frozen, canned, and dehydrated pimiento products were also prepared from the same lot of raw material. Each was used in preparation of standard processed brick pimiento cheeses. The dehydrofrozen product exhibited unusual flavor retention and offered advantages in the manufacturing operation because of its reduced moisture content.

Following these favorable preliminary observations, a pilot-plant run was made by a commercial dehydrator according to directions furnished by the Bureau. Satisfactory results were obtained when the dehydrofrozen pimiento was used in a pilot-plant scale preparation of pimiento cheese.

Vegetable processing problems of the Lower Rio Grande Valley investigated

Considerable difficulty has been experienced by canners of the Lower Rio Grande Valley area in preparing high quality packs of locally grown tomatoes. Tomatoes in this area are customarily grown for "greenwrap" fruit and not primarily for cannery use. Difficulty is experienced in obtaining ripe tomatoes having sufficient depth of red color to yield a high quality canned product. In cooperation with the Texas Agricultural Experiment Station's Substation No. 15, the Fruit and Vegetable Products Laboratory at Weslaco, Tex., is evaluating the canning quality of a number of promising strains of tomatoes which are being selected as suitable for growing under Valley conditions.

Southern peas (cowpeas) are an important canning and freezing item for Texas food processors; however, difficulty has been experienced in processing because the harvested peas vary widely in maturity. Immature peas have less tendency to swell when processed than do mature peas. When cans containing a high percentage of immature southern peas are processed, a slack fill results, whereas the same amount of mature peas will "overfill" the cans and cause loss of texture of the canned product. Laboratory studies indicate that peas of different maturity may be separated by flotation in salt brine of proper density; the immature peas will float and the more mature ones will sink. Peas thus sorted show less variability with respect to can fill than do ungraded field-run peas.

An investigation of the darkening of canned sliced beets has demonstrated that this discoloration is due to inadequate exhausting of the cans prior to sealing. Residual oxygen in the can combines with pigment of the beet slices to produce a dark color. Results of the investigation, with suggestions as to how to avoid the occurrence of discolored beets have been published.

The increased emphasis now placed on problems of vegetable processing by the Bureau's laboratory at Weslaco, Tex., reflects the need

and demand for fundamental and practical technical information to guide the conversion of fresh vegetables to improved processed products.

Morphology and pigmentation of certain yeasts

A 40-page, highly illustrative article depicting some 30 species and strains of yeasts in 12 genera is being published in the botanical journal FARLOWIA (in press). The illustrative material was compiled during the past several years in connection with basic studies on the nature of yeast species responsible for gaseous fermentation of brined vegetable material, and the species responsible for film formation on commercial brines. The work was conducted cooperatively by the Departments of Animal Industry and Horticulture of the North Carolina Agricultural Experiment Station, the Bureau of Animal Industry of the USDA, and this Bureau's Food Fermentation Laboratory at Raleigh, N. C.

The purpose of this unusual publication is to acquaint those interested in the study of yeasts with some of the observations of cooperative investigations on the colonial and cellular morphology of common yeast species (and related types) associated with fermentations in brine. Pigmented species found on the growing cucumber plant (flowers, ovaries, and fruit) are also shown, as well as certain yeasts found in connection with brined meats. Some 34 pages of the article are devoted to pictures, including 12 pages in natural color of yeast colonies and related subjects, and 22 pages of black and white photographs, the majority of which are photomicrographs of yeast cells from different cultural media.

The National Pickle Packers Association made this publication possible by a grant to the North Carolina Agricultural Experiment Station to underwrite the cost of reproducing the photographs, and printing the article. Reprints of the publication will be available from the organizations which cooperated in the study.

New approach to explaining cucumber softening problems

Enzymatic softening of brined cucumbers continues to cause serious economic loss to the pickle industry—amounting to about $2 million each year. Basic microbiological and chemical studies, aimed at establishing the relationship that exists between the naturally occurring microbial flora of the cucumber plant and the occurrence of softening enzymes in cucumber brines, are now in their second year. Three agencies, the North Carolina Agricultural Experiment Station, the Bureau's Food Fermentation Laboratory at Raleigh, N. C., and Harvard University, have cooperated in this study, which has concerned tracing population changes and identifying the principal microbial groups (bacteria, yeasts, actinomycetes, and molds) occurring on the cucumber plant (blossoms, ovaries, and fruit). Studies are based on samples collected from commercial cucumber fields in eastern North Carolina throughout the harvest season.

Special attention has been given to populations and species of higher fungi (molds); later, their biochemical properties, particularly the ability to destroy pectin and cellulose, will be investigated. One or both of the latter characteristics would be associated with any group of microorganisms concerned with softening of brined cucumbers. By use of newly devised cultural and separation techniques, over

1,000 isolates of fungi were obtained during the 1952 season. Identification studies are now in progress in cooperation with mycologists at Harvard University. About two-thirds of the cultures have been studied and species belonging to some 18 genera of fungi have been identified. A number of the species isolated are well known for their ability to destroy pectin and cellulose. Also in the collection are several new fungi, as well as several known species, that are pathogenic to the cucumber and related crops.

Grains

New type of quick-cooking rice

A new form of quick-cooking rice, under development at the Western Regional Research Laboratory, may open larger domestic outlets for this product of American agriculture. When prepared for the table, this new rice product closely resembles ordinary boiled white rice in color, texture, and flavor, but kitchen preparation requires only a few minutes—an important consideration.

Processing operations present no unusual problems. For preparation, milled white rice is soaked in ordinary tap water approximately 45 minutes until it reaches a moisture equilibrium at about 30 percent water content. The free water is then drained off and the wet rice placed in a pressure cooker or retort for 15 minutes under 15 pounds steam pressure. The cooked rice is removed and dried until the moisture content drops to 8 to 10 percent. Detailed additional studies are being made to determine optimum drying conditions. The dried product is allowed to stand for 10 to 12 hours at room temperature to insure uniform distribution of the residual moisture throughout the individual grains. The dried rice is then "expanded" by a 10- to 15-second exposure to a stream of air heated at 480° F., and packaged. Additional work is underway to determine the storage characteristics and shelf-life of this type of rice.

Preparation of the expanded rice for serving is very simple. Salted water is brought to a boil, removed from the fire and the expanded rice product added at the ratio of one cup of rice per cup of water. After a period of 2 minutes has elapsed, or as soon as the rice has shrunk to the normal size of white rice and settled to the bottom of the vessel, the excess water is drained and the rice is ready to serve. Taste panel tests have indicated that the acceptability of the reconstituted product is probably equal to that of standard white rice cooked in the usual manner.

Test for milling quality found applicable to wheat regardless of station and year of growth

The ever-present need for developing new wheat varieties resistant to insects and disease necessitates a continual program of wheat breeding. In the interest of efficiency and economy, breeders require a test by which they can predict milling quality early in the breeding program when only a few kernels are available. The 1952 report described the cooperative work on Pacific Northwest wheats carried on by the Western Wheat Quality Laboratory, Bureau of Plant Industry, Soils, and Agricultural Engineering, and the Western and Northern Laboratories of this Bureau in an effort to develop the desired test.

In 1952 it was reported that the Northern Laboratory had found that the thinner the endosperm cell wall of a variety the better was its milling quality. Additional studies have been made of 4 varieties of Pacific Northwest wheat grown at 3 stations in each of 3 years. Regardless of the station at which the wheat was grown and the year of growth, the thinness of the endosperm cell wall remained generally indicative of milling quality (correlation coefficient=0.82). The thinness of the wall was also found to be directly related to 3 of the 5 factors used to determine milling score—yield of patent flour, yield of straight flour, and milling time (correlation coefficients=0.76, 0.78, and 0.82, respectively). Tempering moisture was uniform for the series. Thinness of the endosperm cell wall was not related to ash content (correlation coefficient=0.30). A variation of 0.7 microns (1 micron equals 39.37 millionths of an inch) in average thickness of the endosperm cell wall was the maximum found in any one variety grown at the 3 stations in 1 year, or grown for 3 years at 1 of these stations. Maximum variation for 1 variety grown at the 3 stations for the 3 years was 0.8 micron. These variations were not significant. The only significant variations found were those between varieties.

Improved procedures for milling rice developed

Improved procedures for milling rice have been developed on a pilot-plant scale and are ready for commercial evaluation. Application of those procedures by domestic mills should result in less breakage of rice grains and a higher yield of whole grain, or head rice. It is possible that the value of milled rice products could be increased by as much as $15 million annually, at present price levels and production.

The investigations were conducted at the pilot-plant rice mill of the University of Arkansas' Institute of Science and Technology at Stuttgart, Ark., under a research contract with the Department of Agriculture. Over 150 samples of long- and medium-grain rice were milled to determine the amount of breakage that takes place in each step of the milling process. Of particular interest is the large amount of breakage in the material as received prior to the milling process, indicating the need for greater care during combining and drying operations.

A study of the use of different types of abrasives, and of the steaming of brown rice showed that these pretreatments did not materially affect the yield of head rice from prime rough rice but did improve yield from heat-damaged rice. The efficiency of the hulling operation and, therefore, the capacity of the plant was increased by these pretreatments.

An investigation of the effect of the temperature and relative humidity of the pilot-plant milling room upon yield of head rice showed that optimum yields of head rice were obtained when the milling room was at a relative humidity of 70 percent. Lower relative humidities resulted in a very marked lowering in yield. For example, there was an increase in yields of head rice of 40 to 46 percent when the relative humidity was changed from 30 to 70 percent at constant temperature. Inasmuch as the relative humidity in the milling room may vary considerably in the course of a season, it is probable that this factor has a significant effect upon yield of head rice and must be controlled to obtain optimum results in milling.

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Data obtained in the pilot plant were checked through the cooperation of several commercial mills. One sample of Rex Ark variety of rice was milled at 55 percent relative humidity and gave a yield of 50.7 percent head rice, whereas at 66 percent relative humidity the yield was 63 percent of head rice. Studies indicated that it is possible to obtain the same results by control of the relative humidity in only a few segments of the rice milling equipment, particularly in the aspirators, instead of in the entire milling room.

In June 1953, a conference of the rice industry was held at Stuttgart, Ark., to review results of this work and to plan for commercial testing of the research findings.

Oilseeds

Gelsoy as a natural bread softener

Gelsoy, a new protein product from soybean oil meal discovered at the Northern Regional Research Laboratory, was discussed briefly in the 1949 report. Recent work has shown its potential use as a bread softener.

When Gelsoy was first developed it was thought that it would be suitable for bakery use as a meringue or topping. However, extensive testing showed that it was not stable enough after baking for this type of application. Subsequently other food uses were investigated under a research contract with Food Technology, Inc., Chicago, Ill. The results of the first phase of this work indicated that Gelsoy has considerable merit for use in bread as a natural softening agent, in frozen desserts, and in sausage for emulsification and stabilization of fat. Additional work is now in progress.

The laboratory's studies on the use of Gelsoy in bread showed that optimum softening action was obtained at the 1 percent level. Gelsoy also increases water absorption and produces a dry, elastic dough which not only lessens operating difficulties in dough-handling equipment, but also reduces the number of unsalable loaves of bread produced. The decrease in bread firmness, resulting from the addition of 1 percent of Gelsoy, is comparable to that attained by use of permissible quantities of other acceptable softeners. Correct use of Gelsoy, as well as other soy flour products, requires addition of small amounts of an oxidizing agent such as potassium bromate to maintain optimum loaf volume, grain, and texture. In contrast to certain synthetic softeners, bread containing Gelsoy has good resiliency, with slices and loaf returning to their original shape after normal deformation. A pilot trial in a commercial bakery, using 500-pound batches of wheat flour, confirmed laboratory studies on the softness, absorption, dough-handling properties, and resiliency of white bread containing Gelsoy.

Studies on toxicity of trichloroethylene-extracted soybean oil meal

The hemorrhagic disease in cattle caused by trichloroethylene-extracted soybean oil meal (TESOM) was discussed in last year's report. With but one exception, plants using trichloroethylene have either shifted to hexane as a solvent or have ceased operations. However, the actual causative agent, an unequivocal test for its detection, and nontoxic processing conditions, have not yet been established. These important problems must be solved before resumption of trichloroethylene extraction of soybeans.

Some evidence has indicated that autoxidation products of trichloroethylene might be responsible for formation of the toxic meal. Purified autoxidation products, including dichloroacteyl chloride and trichloroethylene oxide, have been prepared and reacted with soybean flakes. Assay tests indicate that these meals are not highly toxic and probably not responsible for the toxicity of TESOM in cattle. Meals prepared on a pilot-plant scale using soybeans freshly harvested, were highly toxic, but not appreciably more than meal extracted 4 months later from the same varieties of beans harvested at the same time.

Quantitative studies on toxicity indicate that certain commercial meals are very toxic to calves when fed at the 3 pound per day per 100 pounds of calf weight level, but the same meals may require 300 to 600 days to produce death when consumed at the rate of 1 pound per day per 100 pounds. Other commercial meals have shown considerably less toxicity when fed at the 3-pound level, with typical blood changes occurring in some animals after approximately 500 days. Previously it had been shown that some meals, even when fed at the rate of 1 pound per day per 100 pounds of calf weight, required over a year to produce typical symptoms.

Research on the isolation and identification of the toxic principal and on the assay procedure for its determination is being continued.

Advances in edible spreads of wide plastic range

The low-temperature limit at which butter and margarine can be spread on bread ranges between 40° to 65° F., depending on the particular butter or margarine. If stored at lower temperatures, these products must warm and soften before they are satisfactory for table use; at higher temperatures they melt and separate into water and fat layers. For this reason the Armed Forces have expressed need of a spread that would be equally acceptable to a soldier in the desert heat or the Arctic cold. Consequently, the Quartermaster Food and Container Institute for the Armed Forces invited studies on this problem.

The Northern Regional Research Laboratory's development of a spread containing vegetable oils, monoglycerides, vitamins, flavoring, and surface-active agents, and which can be readily spread on bread at temperatures from 0° to 110° F., was discussed in last year's report. Tests at the Quartermaster Food and Container Institute indicated that initial samples were probably acceptable but that considerable improvement needed to be made in "acceptance level" and storage stability. Accordingly, studies were continued to find ways and means of improving these factors. Improvement of plastic properties in bread spreads resulted when treatments were employed that assured the formation of small crystals properly dispersed in the spread. Taste panel tests indicated decided improvement in mouthing qualities and "get-away." The treatments also gave softer spreads at low temperatures. By proper use of antioxidants, protecting the spread during processing, packing it with an inert gas, and treating it to improve "get-away," a superior product has been obtained. Combinations with butterfat also improved the "acceptance level."

The Southern Regional Research Laboratory has also developed a product which is spreadable, stable, and palatable over a wide temperature range. This product is prepared from hydrogenated (hardened) cottonseed oil and aceto-olein—a "tailormade" fat product—

and has almost constant consistency or spreadability at temperatures from 5° to 120° F.

The spread, as prepared, contains 79 percent aceto-olein product, 18.5 percent highly hydrogenated cottonseed oil, 2.5 percent finely ground salt, and traces of antioxidant, butter flavoring, and butter color. Ingredients are mixed at a temperature just below the melting point of the hard fat and chilled to 0° C. while being worked or mixed. The resulting product resembles ordinary margarine in appearance and taste, but contains no moisture or protein solid to promote spoilage by hydrolysis or bacterial action. Experiments are in progress to ascertain whether the aceto-olein products are suitable for edible purposes. Tests thus far completed have shown every evidence of acceptability.

Acetostearins—new tailormade fats—in commercial pilot-plant production

Acetostearins, new tailormade fats developed from research conducted at the Southern Regional Research Laboratory, are available from a commercial company in pilot-plant quantities for investigation and evaluation.

Completely solidified natural fats are rigid crystalline materials and will not exhibit plastic flow under stress. They can be made plastic only by first breaking the crystals, then lubricating the particles with a liquid oil. Ordinary plastic fats like shortening contain 75 to 95 percent of liquid oil at room temperature. Films formed of such plastic composition are greasy to the touch and will lose liquid oil to most materials coming in contact with them.

Solid products having the unusual property of being both nongreasy and plastic were produced from the chemical combination of acetic acid with mono-gycerides in a mixture of mono-, di-, and triglycerides derived from ordinary hard fats. Initial work on products of this type was reported in 1951. These acetic acid containing fat products, which have been classed under the general name of acetostearins, seem to offer opportunity for extended utilization of fats and oils and to provide for new developments in the handling of food products. For example, these materials can be considered for use as coatings for meat products, cheeses, fruits, and nuts. Tests made thus far to demonstrate their edibility have indicated that they will probably be satisfactory. For use in another field, acetostearins and related substances, known as aceto-oleins, were evaluated as plasticizers. Combined with vinyl chloride resins they were satisfactory as a secondary plasticizer; with a material such as tricresyl phosphate the resin quality was improved; and combined with dioctyl sebacate, a premium-quality plasticizer, they were suitable as extenders.

In January 1953, the Glycerine Manufacturers Association gave the team which conducted this research an award for an outstanding accomplishment in the application of glycerine and glycerine derivatives.

Processing conditions determined for optimum quality in peanut butter

Research to determine the exact effect of processing conditions on the quality of peanut butter, reported in 1951, has continued and the preliminary results described have been confirmed. Butters prepared

from peanuts roasted under widely different conditions have been evaluated immediately after preparation, and periodically during storage at 80° F. for 2 years. Data indicate that for practical purposes the shelf-life of peanut butter, is sufficiently long to permit normal distribution and handling before the product acquires off-flavor or odor.

Stored peanut butter retained acceptable odor and flavor characteristics for a year or longer. During storage for more than a year some butters developed objectionable flavors before appreciable oxidative rancidity could be detected by tasting or chemical tests. Medium roasted butters were given satisfactory ratings for odor and flavor when stored as long as two years, but both light- and heavy-roasted products received unsatisfactory ratings after approximately 1½ years of storage. Off-flavors from staling occur well in advance of organoleptic rancidity.

Chemical examination of oils contained in these peanut butters indicated that rancidity did not develop to any troublesome extent even after storage for as long as 2 years. There was no correlation between color or degree of roast to which the peanuts had been subjected and the keeping times of oils extracted from peanut butter either freshly prepared or stored for a length of time. This research has been concluded and results are being prepared for publication.

Improvements sought in rapidly changing technology of the cottonseed industry

Cottonseed is processed commercially by three methods—hydraulic pressing, screw pressing, and solvent extraction. Hydraulic pressing accounts for 50 to 55 percent of the total seed processed, and the remainder is divided about equally between screw pressing and solvent extraction. Recently new types of solvent processes have been introduced. Some of the results obtained by the Southern Regional Research Laboratory in continuing progress to satisfy industry needs in applying the different processing methods are reported below.

Processing data to improve hydraulic pressing of cottonseed has been developed at the Tennessee Engineering Experiment Station under a research contract with the Southern Laboratory. Results indicate the possibility of reducing residual oil in hydraulic press cake about 0.5 percent below the current average mill values. This would mean an increase in cottonseed oil production of 5 pounds per ton of seed crushed or 5 million pounds for an average season's crush. At current prices this would add at least $500,000 per year to the value of the products of hydraulic pressing.

Improvements in oil extraction on a laboratory scale were obtained, using cakes with a thickness of 1 inch or less, by raising the temperature of the cake to 210° F. and applying a pressure of 2,000 pounds per square inch (p. s. i.) for 35 minutes. Oil quality was not adversely affected by pressing temperatures as high as 230° to 245° F. To obtain optimum results, pressure should be applied slowly to reduce residual oil content of cake, hull content should be kept as low as possible, cooking at high pressures and temperatures should be avoided, and cake moisture should be adjusted to about 6 percent. Mill tests show excellent agreement between the laboratory work and large scale tests carried out in cooperation with a commercial mill.

Results obtained in a study of the screw pressing of cottonseed by the Engineering Experiment Station, Texas A. and M. College, under a research contract with the Southern Laboratory, show that screw-press mills processing cottonseed with inadequate rolling and cooking capacity can improve their operations by increasing these facilities.

Other conclusions of the study which have practical applications are:

Using cottonseed meats of the highest protein content consistent with good separation will result in increased capacity and maintain products of high quality and oil yield. A better quality of oil is produced from thinner rolled meats. It is important to have sufficient moisture in the upper rings of the cooker to avoid high residual oil content of cake, but the final moisture content of the cooked meats should be around 3 percent. For most mills, about 1 hour in the cooker should be right to obtain this percentage of moisture. The proper speed for hard pressing is about 1 revolution per minute on the main screw when the rate of cottonseed crushed per machine is 1 ton per 24 hours. Load on the screw press motors is a measure of press efficiency. Efficiency can be increased by more thorough cooking, proper moisture adjustment, and increasing the rate of feed. If the oil cooling method is employed, sufficient cooling capacity should be provided to reduce the temperature of the largest volume of cooling oil expected to below 120° F. Screw press oil should not be stored for long periods of time without refining. Extended storage of oil, if it cannot be avoided, should be at the lowest practical temperature that can be maintained in the storage tanks. Factors which most affect the yield of refined oil were: The power applied per ton of cottonseed during screw pressing, preparation of the meats, and quality of the seed processed. Maintenance costs depend principally upon cleanliness of the seed. The wear on the processing machinery was found to depend upon the amount of power applied and to be independent of the screwspeed employed.

Process development research at the Southern Laboratory has demonstrated that the filtration-extraction process for cottonseed, described in the 1952 report, can be used also for soybeans, rice bran, and flax. The excellent results obtained in processing these oil-bearing materials indicate that this new process may meet the need for a direct solvent extraction process which is versatile and readily adaptable for quick conversion from one oilseed material to another.

Seven engineering firms have obtained licenses from the Department of Agriculture to practice the filtration-extraction process under a pending Bureau patent, and three of these firms have designed plants for using this process, based on results obtained by the Southern Laboratory in pilot-plant research. Nine other processors are cooperating with the Southern Laboratory in commercial development of the process for various other oilseeds and oil-bearing materials.

Preliminary experiments have been conducted on the application of this process to sesame, peanuts, and milo germ. Results indicate that the same rolling, cooking, and reforming equipment can be used. However, for each oilseed or oil-bearing material it was necessary to establish optimum conditions for rolling, cooking, and reforming operations to convert the material into a granular form in which the fines are consolidated into larger agglomorates. Such material has desired

characteristics for an efficient filtration-extraction operation—rapid extractability of oil, particles of optimum shape and size distribution, and relatively high incompressibility.

Recent investigations of cottonseed processing at the Southern Laboratory and cooperating organizations have indicated the need to reexamine and further study the effect of processing conditions on product quality. As basis for a research program to improve quality of the meal and to maintain optimum quality of the oil, fundamental differences between various processing conditions for each individual process were determined.

A systematic investigation of hydraulic and screw press meals from 5 commercial mills showed basic differences between the 2 processes and in the quality of the products. Results on a limited scale indicated that screw pressing results in more pigmentation, particularly gossypol pigments, in the oil than does hydraulic pressing. Free or uncombined gossypol content of meal, which determines the extent of its usefulness for unrestricted feeding to growing chicks and swine, is generally lower in screw pressed meals than in hydraulic pressed meals. These investigations are proving very useful in determining the advantages and limitations of present commercial products and in directing research designed to improve their utilization.

Poultry and Dairy Products

Proposed process for treatment of dairy waste

Research on the development of simple waste-treatment plants designed to minimize stream pollution by effluent from milk-processing plants, has continued at the Eastern Regional Research Laboratory with excellent results. Previous studies had shown that a mixed culture of microorganisms could be developed which would oxidize these wastes with great rapidity and at the same time convert about half the organic solids in the waste to microbial cell tissues. Further work has shown that the rate at which these cells oxidize their own tissue is extremely low; about 3 to 4 parts per million of oxygen are consumed per hour. This rate of oxygen uptake is lower than the normal reoxygenation rate of a flowing stream. Therefore, discharge into the stream of an effluent containing these cells would not cause a serious oxygen deficit, even when the volume of effluent is large in comparison with the stream flow.

On the basis of laboratory results a design has been developed for an extremely simple one-tank aeration system specifically adapted to treating milk wastes. A pilot plant study of this process is being carried out by contract with the Pennsylvania State College where 10,000 gallons of waste from the creamery are treated daily in an experimental unit. Under a second contract the effect upon the chemical and biological makeup of the stream, of the discharge of (1) untreated milk waste, (2) milk waste treated by the conventional process, and (3) cells produced by the proposed process, is being studied under field conditions. If successful, this research will furnish the basis for full scale design of treatment plants. It is anticipated that the contract studies will be completed by the end of 1954.

A rapid and simple method for measuring the efficiency with which aeration devices transfer oxygen to solutions was also developed.

This method should be of value not only in the design of waste treatment plants but in testing the efficiency of aerators in other oxidative fermentation processes such as production of antibiotics and vitamins by aerobic fermentation.

Further improvements in quality of whole-egg solids

In 1950 the Bureau reported that research at the Western Regional Research Laboratory during the 2 preceding years had established the cause of the most serious type of deterioration suffered by egg solids (whole-egg powder) during storage at high temperatures. It was identified as the reaction between the small amount of glucose normally present in the egg and certain nitrogenous constituents, especially the phospholipid cephalin. Complete removal of this glucose from the egg magma before drying, by means of a brief yeast fermentation, prevented subsequent occurrence of this reaction and greatly improved storage life of the egg solids.

Further research, much of it carried on in cooperation with industry and the Quartermaster Food and Container Institute, has greatly broadened these findings. Within the past 3 years the cumulative advances, now fully demonstrated on an industrial scale, have quite reversed the gloomy outlook for "dried eggs" which prevailed in 1948. Egg solids are now used commercially with excellent results in such products as prepared baking mixes, noodles, dessert mixes, and frying-batter mixes, and the stringent requirements for acceptability of egg solids as a military ration item can now be met without question.

Recent Bureau research has included the determination of optimum conditions for removal of glucose from whole-egg magma, both by the fermentation process and by treatment with an enzyme preparation (glucose oxidase) which converts glucose to inactive substances; comprehensive evaluations of the storage stability of egg solids as affected by the many processing and storage variables; and development, cooperatively with processing plants, of practical procedures for manufacturing the improved powder.

The yeast and enzyme methods for removal of glucose were found to be generally equivalent in quality, and in ease of plant operation and control. However, for reasons not yet understood, atypical off-flavors occasionally develop during storage of powders prepared by the yeast method. In the enzyme method, hydrogen peroxide plus the enzyme catalase—used to supply oxygen—do not adversely affect either initial quality or storage stability. In cooperation with the Food and Container Institute, a comprehensive storage stability test was conducted. "Stabilized" egg powder, manufactured by the acidification process described in the Bureau's report for 1946, was compared with glucose-free powder. The initial moisture content was 2 percent in both cases. Consumer-type preference and acceptability evaluations were made on all samples. Initially the tasters reported a slight preference for the glucose-free powder. Both varieties held up well for 1 year at temperatures of 40° and 70° F. At 100° F., however, the acidified powder browned noticeably after only 3 months, while the glucose-free powder showed no browning after 1 year. Consistent with this evidence of a difference in stability, preference of the panels for the glucose-free product became more pronounced as the period of high-temperature storage increased. The Food and

Container Institute has now issued tentative specifications for procurement of glucose-free egg solids.

Present efforts are directed toward acquiring information on the nature of the oxidative deteriorations, which, although not as rapid or conspicuous as those involving glucose reactions, still limit the utilization of whole egg solids in some potentially important outlets.

High temperature scalding for turkeys evaluated

The most important change in commercial poultry processing during the past several years has been a trend from a scalding temperature of about 126° to one of 140° F., in order to reduce costs and provide a product free of pinfeathers. This change has created uncertainties and possible hazards in the processing and frozen storage of poultry, especially of turkeys, which lose quality more rapidly in storage, and yet are often stored longer than chickens. In studies at the Westen Regional Research Laboratory, high temperature (140° F.) scalded turkeys have been found acceptable in practically all respects when moisture loss from the surface is prevented or minimized throughout the life of the product.

Processing and frozen storage tests were conducted with turkeys scalded at 120°, 122°, 126°, 129°, 132°, and 140° F. Variations in scalding time, chilling method, and packaging were investigated. In addition, an objective laboratory method for determining commercial efficiency of feather removal was established and now the effects of various combinations of slaughtering procedures, scalding temperatures, and scalding times upon feather removal can be evaluated without recourse to inconvenient and expensive large-scale experimentation. The method consists of a determination of the average force required to pull out individual body feathers.

Tests showed that higher temperature scalds permitted complete removal of feathers by commercial facilities at greatly reduced labor cost, but also resulted in removal of the cuticle (outer layer of skin) of the turkey. In the ranges studied, duration of scalding is much less critical than temperature. Consequences of the loss of the cuticle layer are: Shiny, pink, clean appearance; much greater susceptibility to dehydration and darkening on exposure to air; and wrinkling and toughening of skin when bird is roasted.

Moisture losses in the unpackaged turkeys were directly correlated with scalding temperature. Without adequate moisture control, either chilled or frozen storage resulted in rapid deterioration of appearance to an unacceptable level. However, turkeys scalded at 140° F., eviscerated and packaged in sealed bags, lost practically no moisture in 12 months' storage at −5° F. and were acceptable in appearance. High temperature scalding had no effect on rancidity development during frozen storage, or on tenderness of the roasted muscle. Toughening of the roasted skin was found to be correlated with scalding temperature, however, this can be reduced considerably by covering the turkey with oiled cheesecloth during the roasting period.

Results indicate that turkeys scalded at 140° F. have a different appearance but are acceptable for frozen storage if proper moisture control is maintained by humidified chilling, moisture impermeable packaging, or other means.

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Problems connected with high temperature scald that still lack a complete solution, such as the prevention of toughness of the roasted skin, will continue to be studied.

Sugars, Sirups, and Honey

Research continued on expansion of honey utilization

The Eastern Regional Research Laboratory's program to find new uses for honey and expand existing uses, is continuing. The increased importance of crop pollination by honeybees is a driving factor in the search for methods to increase the consumption of honey and thus help to maintain adequate pollination. Progress has been made along the following lines.

Research on new food uses for honey at the laboratory had developed a fruit and honey spread which depends upon fine-grained dextrose crystallization for its smooth texture. This product, attractive to many who do not care for honey alone, is now made commercially by a western honey packer.

A broad study of the role of honey in commercial baking has been carried out at the Kansas Agricultural Experiment Station under two contracts supervised by the Eastern Laboratory. Studies have covered the field from white and whole-wheat breads, yeast-raised sweet goods, cakes, and fruitcake, to the principal types of cookies. Distinct advantages in flavor and keeping qualities result from the use of honey in many of these baked goods. The effect of variations in honey sources and of their physical and chemical properties upon the quality of the baked goods, has also been examined. Publications describing this work list the types of honey found most suitable for various baking applications.

In an effort to obtain more information on the changes that take place when nectar is converted to honey, a study was made of the action of the honey enzyme, invertase, upon sucrose. Six sugars other than sucrose and its hydrolytic products, glucose and fructose, were found in this reaction. Of the six, the sugar found in largest amount was isolated and its structure found to be α-maltosyl- β-D-fructofuranoside, a new trisaccharide. It appears likely that this sugar is produced by enzyme transfer of a glucose molecule resulting from sucrose hydrolysis, to an intact sucrose molecule.

Preliminary work on the application of carbon column adsorption to the quantitative analysis of honey sugars indicates that this may be a useful procedure in the study of this complex mixture. Results show that in many cases over 98 percent of the dry substance of honey may be accounted for as sugars, rather than the 94 to 95 percent found by conventional methods of analysis.

Plastic bags prevent spoilage of maple sap

The quality, color, and flavor of maple sirup are greatly influenced by the care used in handling the sap and boiling it to sirup, and more particularly by the degree of microbial fermentation of the sap. With the exception of exercising scrupulous cleanliness and rapidity in handling sap, there has been no method available which would effectively control microbial deterioration of maple sap throughout the season. During the latter part of the sirup season when sap becomes

discolored, milky, ropy, or sour due to growth of microorganisms, the sirup produced is of lower quality.

Recently a plastic sap bag has come into use to replace metal or wood buckets. The Eastern Regional Research Laboratory has found that these bags are sufficiently transparent to the sun's ultraviolet radiations to keep the sap essentially sterile, and to sterilize that which has become contaminated. This sterilization is most effective when the bags of sap are exposed to bright sunlight during cool weather. Since growth and destruction of the bacteria are occurring simultaneously in the exposed bags, predominance of one process over the other is dependent upon such factors as temperature, amount of sunlight, and time of exposure. This is the first time a means has been demonstrated which will help provide a continuous supply of unspoiled sap throughout the season.

Oil-firing evaporator makes more uniform maple sirup, reduces labor, increases capacity

With the increasing scarcity and cost of wood and labor to operate the maple sirup evaporator, use of oil as fuel is becoming more and more desirable. Another advantage is that the constant and steady heat of the oil fire tends to give a nonvarying rate of evaporation, making it easier to produce sirup of more uniform quality. Experimentation at the Eastern Regional Research Laboratory with various designs of oil furnaces on small farm-type evaporators also showed that an evaporating capacity at least 30 percent greater than the manufacturer's rating for wood could be obtained. The greater the evaporation rate in a given pan, the faster the sap passes through the pan and hence the lighter the sirup color. Long heating is a major cause of dark color.

In the development of an oil-firing evaporator, the ordinary wood-burning firebox was found unsuitable. The new design, evolved by experimental trial, is longer, deeper, and equipped with a burner similar to the standard "gun" type of house-heating burner and using No. 2 oil. With this design, an average of 10 gallons of sap is evaporated per gallon of oil.

For an evaporator which would handle 200 gallons of sap per hour, the entire equipment, including oil burner, brick and storage tank, could be purchased for about $1,000. Cost calculations show the total cost (including labor) to be about the same for oil as for wood. However, as wages rise and wood becomes scarcer, the comparison of cost will become more favorable to oil, and the principal advantage of oil as a fuel—uniformity and better quality of sirup—is always present.

Use of ion-exchange resins in sugarcane processing

Different types of special resins, known as ion-exchange resins, will remove either acids or bases from solution when neutral substances such as common sugar are also present. A number of beet sugar factories have employed this method for removing mineral impurities in juices prior to the crystallization step and have obtained an increase in yield. In use of the conventional ion-exchange resins which have been available, it is necessary to cool the juices to avoid loss of sugar by inversion. Since beet sugar factories are located in cool climates the juices can be chilled economically during the winter processing

season and the resins used to advantage. Although cane sugar factories have been interested in the use of these resins, the loss by inversion which occurs with the conventional ion-exchange system at the warm temperatures where the industry is located offsets any gain in sugar recovery resulting from the elimination of minerals. The cost of mechanical refrigeration of the large volumes of clarified juices which are produced also offsets any gain in sugar recovery.

With the recent perfection of new types of ion-exchange resins that are strong enough bases to separate acids from their salts, it has been possible to devise a reverse cycle procedure in which the juice does not become sufficiently acid at any time to cause inversion of sugar. This method, carried out simply by passing the juice through a strong acid-removing exchanger and then through a weak base-exchanger that readily removes free bases, provides for simplicity of operation and is better than methods in which the exchange resins are mixed and must be separated for regeneration and re-use. Synthetic solutions with the composition of sugarcane juice, actual clarified juices obtained in pilot-plant processing experiments, and reconstituted juice prepared from clarified juice sirups, have all been purified by this procedure with negligible amounts of inversion.

In addition to removing mineral acids and bases present, these exchangers also remove natural organic acids such as aconitic and aspartic, nitrogen-containing impurities, and color. The study also included an examination of a variety of suitable acid- and base-exchangers in various combinations, a determination of their efficiencies, and the optimum cycle for operation of the process.

Practical tests of this promising technique are planned during the processing of the 1953 Louisiana sugarcane crop. It should greatly improve efficiency of the bone char refining step and should also increase the amount of sugar recovered. The improved quality of sugar thus obtained may provide a solution to the problem of sediments or flocs in bottled carbonated beverages.

Foods—General

Stabilizing dehydrated foods by in-package desiccation

Dehydrated vegetables of good to excellent quality can now be produced commercially but many of these products deteriorate significantly before they are consumed, particularly if high temperatures are encountered during transportation and storage. The storage stability of dehydrated vegetables under these adverse conditions, can be markedly improved by lowering the moisture content below that usually obtained in commercial operation. However, to achieve extra dryness through prolonging the normal drying operation in tunnels or bins tends to impair quality and to increase costs substantially.

During World War II the Western Regional Research Laboratory found that if the conventionally dehydrated vegetable is packaged with a small sack of a desiccant, such as calcium oxide, additional moisture is gradually removed from the product and its storage life is extended several-fold. This process, known as "in-package desiccation," has recently received renewed attention at the Laboratory.

In-package desiccation gave marked protection to dehydrated cabbage, a product very susceptible to browning, during 6 months storage

at 100° F.—a very severe test for this type of product. Although somewhat less efficient than calcium oxide as a desiccant, montmorillonite (a special type of clay) was also found effective, and has the advantage of not swelling during hydration. Data were obtained which make it possible to estimate the amount of montmorillonite required to achieve a given reduction in the moisture content of dehydrated cabbage.

In-package desiccation with calcium oxide has been adapted for use with various fruit juice powders prepared by the Western Laboratory's puff-drying process. Such extra protection, used in the semicommercial production of orange juice powder, adequately protects flavor, odor and color, and prevents caking.

A commercial two-way-stretch paper has been found to have desirable permeability and mechanical properties for use as the desiccant container. It can be fabricated into bags which can be filled on automatic, high-speed, heat-sealing equipment. Such packets would have a cost advantage over the composite cloth and paper bags required by the military specification developed during the war.

The rate at which moisture is transferred from the dehydrated food to the desiccant depends upon: The nature of the product; temperature; kind, size and shape of container; type of desiccant and its location in the container; and other factors. In cooperation with the University of California, basic data on the rates of moisture transfer were obtained for dehydrated potato dice, potato granules, cabbage shreds, carrot dice, and orange juice powder. This information makes it possible to estimate how rapidly a product will be dried to a safe moisture level under a given set of conditions.

Industry interest has been stimulated by the demonstration that dehydrated foods can be kept in good condition for substantially longer periods with the aid of in-package desiccation.

Precooked frozen desserts

Among the most serious problems of the precooked frozen food industry are those concerned with the maintenance of texture stability in foods containing cooked egg, starch, or flour. Previously, it had not been possible to market satisfactory precooked frozen desserts because of the curdled appearance of the product or the separation of liquid on thawing.

Discovery of the superiority of waxy rice flour for use as a thickening agent for frozen sauces and gravies, reported by the Bureau in 1951, suggested investigation of its usefulness for improving texture stability of frozen pudding and custard-type desserts. The differences in behavior between thickening agents from common and waxy cereals, as well as the differences among the various waxy cereals, are attributed to the higher proportion of branched starch molecules and to variations in molecular size and degree of branching of the waxy cereal starches.

Studies at the Western Regional Research Laboratory have recently shown that pudding and custard desserts are stable to freezing and to storage for limited periods when prepared by substitution of waxy rice flour for part or all of the usual thickening agents. For the cornstarch pudding type of dessert, waxy rice flour has been substituted for the cornstarch and gelatin formerly added, to give a soft gel structure. For the custard type of dessert, part of the egg has been replaced

with waxy rice flour. The separation and curdled appearance that occurs even without storage of frozen products prepared by the usual formulas can be prevented by use of waxy rice flour for storage (0° F.) periods of 6 to 9 months for pudding-type desserts and 2 to 4 months for custard-type desserts. Inclusion of chocolate in a formula containing waxy rice flour and gelatin decreases slightly the storage stability of the frozen product, presumably because of the starch content (8 percent) of the chocolate.

When stored at −10° F., both plain and chocolate puddings containing waxy rice flour show no visible change in appearance when thawed after 14 months. At a storage temperature of +10° F., however, retention of stability is limited to a storage period of less than 1 month. The methods developed for producing stable desserts of the pudding or soft-custard types are adaptable to formulation of cake and cream puff fillings that should also be stable to freezing and frozen storage.

Yeast and oat products lengthen shelf life of candy

The shelf life of several popular candies containing dairy butter can be at least tripled by adding yeast or a special oat flour to avoid spoilage caused by oxidation of the fat. The experimental work in which the new candy recipes were developed was conducted cooperatively by the National Confectioners Association and the Bureau's Southern Regional Research Laboratory.

When butter candies are stored for several weeks or months, particularly at summer temperatures, the butterfat becomes so rancid that the candy is unsalable. Unfotunately, butter does not naturally contain a substance, commonly referred to as an antioxidant, that will retard fat deterioration. Addition of about 3 percent of oat flour or debittered brewers yeast (both known to contain antioxidants) to the butter will give a candy possessing adequate shelf life. In this range of concentration the added products do not impart detectable flavors in most candies.

Candies prepared with brewers yeast and butter will remain free of rancidity 3 to 6 times as long as those made without yeast. Fudge and butter creams, even at a continual storage temperature of 86° F., were protected by yeast for 16 to 19 weeks, whereas the unprotected creams were noticeably rancid in 2 to 3 weeks. Standard butter mints kept only 8 to 9 weeks. With yeast or oat flour they remained free of oxidative off-flavor for 16 to 19 weeks. These findings could be an important factor in increasing the outlet for dairy butter in confections.

Feeds—General

Addition of animal fats or vegetable oils improves alfalfa meal

Manufacturers, handlers, and users of alfalfa meal are constantly plagued by extreme dustiness which presents a constant fire hazard and significant meal loss. Reduction of dust by application of oil has been attempted commercially, but has not been in general use because of its high cost and the intricacy of the oiling equipment. Preservation of carotene by addition of an antioxidant dissolved in oil, as reported by the Bureau in 1951, has logically led to development of satisfactory equipment and methods for oil application.

Recent studies at the Western Regional Research Laboratory have shown that addition of 0.5 to 5.0 percent of vegetable oils or animal fats to dehydrated alfalfa reduces dustiness, gives a greener color, and slightly increases the stability of vitamin A. Several crude or refined vegetable oils, such as cottonseed, soybean, corn, or rice-bran have been found suitable for application when reasonably free of sludge or waxes. Both white and yellow animal greases can also be used.

If an amount of oil in the range of 2 to 5 percent is used, dustiness is reduced sufficiently. The protective effect of oil on carotene (the precursor of vitamin A) is illustrated by one group of experiments with storage at an elevated temperature (65° C.). After 14 days of storage, 80 percent of the original carotene content had been lost from unoiled meal, while only 60 percent was lost from meal to which 5 percent white grease had been added. Different oils appear to have somewhat different protective effects for reasons not yet fully apparent. No evidence of rancidity has been seen.

Acidulated cottonseed oil soapstock, or vegetable oils and animal tallows containing more than 5 percent free fatty acid, cause some loss in green color and should not be used.

Equipment for the application of oil has been developed and consists of a filter and gear pump with a variable-speed drive. The pump and drive are totaly enclosed and can be operated continuously under dusty conditions. Provision is made for continuous variable-speed operation to insure proper oiling when variations in the rate of alfalfa meal production are encountered. The equipment can be procured and installed for a few hundred dollars.

An increasing number of dehydrators, blending firms, and feed manufacturers are applying oil to alfalfa meal. Soybean and rice oils have been in greatest use for they have the advantage of remaining fluid in cool weather. However, animal fats are being used to an increasing extent and this new development would, of course, help to relieve the current oversupply. Treatment of all currently produced alfalfa meal with 2 percent of oil would require approximately 25,000 tons of oil or animal fats per year.

Cheaper and more effective feed supplements evaluated

The cost of producing meat has recently been materially reduced by the introduction of new feed supplements rich in antibiotics or vitamins. The use of vitamin B_{12} supplements—made possible through the large-scale industrial growth of certain microorganisms—has permitted substitution of plant protein for animal protein in feeds without sacrificing rate of gain in weight, efficiency of conversion of feed to body weight, and without increasing the mortality of eggs or young. The still more recent introduction of antibiotic feed supplements has had similar effects through control of mild and ill-defined disease conditions. In addition, the supplements are believed to reduce the microbial population in the intestinal tract which in turn reduces the competition offered to the animal's utilization of available nutrients. The wholesale value of antibiotic feed supplements now used in the United States is estimated to be as much as $18,000,000 annually.

In the search for better and more economical feed supplements carried on at the Western Regional Research Laboratory, attention has

centered on the *Bacillus* group of bacteria, as many strains of this genus may be grown rapidly on inexpensive materials, and the bacterial cells recovered economically in centrifugal yeast separators. Under contract with the Wisconsin Alumni Research Foundation, such bacterial preparations are being tested to determine the feeding response of chicks held on a practical basal ration that contains all known nutritional essentials, but no antibiotics. This empirical screening program is aimed to yield new antibiotic supplements which may be more economical to produce than those available at the present time. Supplements rich in new growth-promoting agents of a completely unrecognized nature may also be found.

The first phase of the program, now virtually complete, has involved feeding tests with approximately 150 stocks of *Bacilli* which have been selected from approximately 2,000 antibiotically-active fresh isolates or stock cultures. After 10 weeks of feeding, six of these stocks have given 5 to 10 percent better chick-growth rates than the basal ration. For ready control of supplement potency, studies are in progress on the fractionation and isolation of the chemical agents involved in these growth responses.

These new supplements will have to be further evaluated in field tests under practical conditions. Through the cooperation of other Federal and State research agencies, it is expected that feeding tests with swine and other animals will be made using supplements which initial investigations with chicks have shown to be of most promise.

Increased application shown Bureau process for synthesizing vitamin B_{12}

Increased use of the Northern Regional Research Laboratory process for making vitamin B_{12} with *Streptomyces olivaceus* was recorded in 1952. The number of domestic firms using the process has increased to seven and the value of resulting production is about 6 million dollars. Roughly, it accounts for 50 percent of the total vitamin B_{12} concentrate used in poultry and swine feed. Use of the fermentation process has extended to one foreign country for broiler feed supplementation. In the broiler industry of the United States, incorporation of vitamin B_{12} in rations is reported to have returned $50 million.

Further research, conducted in large-scale fermentors, demonstrated the versatility of *S. olivaceus* and of the fermentation process for producing vitamin B_{12}. The organism was shown to be capable of utilizing a variety of soybean oil meals, distillers' solubles, cottonseed oil meal, etc., as its source of nitrogen. The importance of this is obvious in view of the changing availability of such products because of regional or seasonal conditions. Fermentations conducted in the laboratory, as well as those conducted under commercial conditions, have shown that media may be sterilized by the continuous or batch sterilization systems without effect on yield of the vitamin. Investigation of the effect, on yield, of various metals used in the construction of fermentors showed that only copper is toxic. However, the adverse effect of this metal is evident only when fermentation media are heated or sterilized in its presence.

FIBERS AND FIBER PRODUCTS

Cotton

Treated cotton cloth of improved durability now available for shading tobacco fields

A lead-chromate treatment developed at the Southern Regional Research Laboratory to make cotton shade cloth more resistant to sunlight was reported in 1949. Later reports announced successful field trials of experimentally treated cloth by Florida tobacco growers. News that the treated cloth had reached limited commercial production and had been purchased by one grower in sufficient quantity to cover a 10-acre field soon followed.

The cloth covering this field served satisfactorily during 1952, its second season, and was again used in 1953. An additional million square yards of treated cloth was in service this year in north Florida. Connecticut Valley tobacco growers, who normally use untreated cloth for only one season, used about 50,000 square yards of treated cloth satisfactorily in 1952, and are using the same cloth in 1953. Commercial finishers have overcome earlier difficulties in treating this type of wide fabric, and can now supply any demand.

It is estimated that if the treated cloth becomes widely used, some 24 million square yards of new cloth will be needed to supply each season's total requirement of about 72 million square yards. Treated fabric costs only slightly more than the untreated. In addition to staving off the danger of losing this market to man-made fibers, general use of lead-chromate treated cloth will result in potential savings of more than a million dollars a year to tobacco growers in the north Florida area.

Potential usefulness of cotton increased by reducing content of crystalline cellulose

Some of the shortcomings of cotton fiber in certain markets are attributed to its large percentage of crystalline cellulose. High crystallinity implies a closely organized arrangement of the cellulose molecules and is associated with such desirable properties as high strength and resistance to heat and moisture. However, high crystallinity is not advantageous where impact strength, toughness, and large extensibility before break are desired for industrial products such as tire cord and conveyor and transmission belts.

The Southern Regional Research Laboratory has developed a treatment which markedly reduces crystalline cellulose without loss of natural fiber structure or the desirable physical properties already possessed by cotton. This decrystallization treatment results in a cotton fiber which is tougher, more extensible, more absorbent, and which has a higher dyeing capacity and greater chemical reactivity than ordinary cotton. The higher reactivity should facilitate further modification of cotton by chemical treatments.

The crystallinity of cellulose is attributed to the hydroxyl groups projecting from the cellulose chain molecule (there are three hydroxyl groups for each glucose unit in the molecule) that participates in the formation of hydrogen bonds. Of those chemical compounds investigated for their ability to break or loosen the hydrogen bonds, an-

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hydrous liquid ethylamine—a chemical closely related to ammonia—was found to be the most useful. Without destroying or damaging the fiber, it reduces the crystalline cellulose from 80 to 90 percent in the native fiber to 20 to 30 percent in the treated fiber. Conditions of treatment which bring about these changes consist in immersing either raw or processed cotton in the liquid amine for a short time, pouring off the excess, washing the cotton thoroughly with an organic solvent—such as cholorform or hexane—and drying. A public-service patent has been obtained on this process.

In these investigations, crystallinity was determined by measuring the relative rate of acid attack on the crystalline and amorphous portions of the cellulose, and qualitative confirmation of the results was obtained by use of X-ray diffraction.

Pilot-plant equipment has been installed to produce larger quantities of decrystallized cotton for further modification to improve resilience and elastic recovery, to obtain engineering data, and to study the economics of the process. Continued laboratory research will include an investigation of other agents that may reduce crystallinity still lower.

New roving twist formula aids in processing cotton

A new formula has been developed by the Southern Regional Research Laboratory for determining the proper twist (number of turns per inch) required in cotton rovings to obtain improved processing efficiency and improved quality of resultant yarns. The new formula incorporates, for the first time, the effect that fiber fineness, staple length of the cotton, and size of roving, have on the amount of twist. Based on the formula, a practical guide known as a nomograph has been constructed to enable rapid determination of the twist required for a wide range of sizes of carded rovings when the fineness of the cotton fiber (as determined by the Micronaire) and the classers' staple lengths are known. Copies of the nomograph are available from the Southern Laboratory and many have already been distributed to cotton processors. This new formula is based on a study of the relation of fiber fineness to the physical properties of single yarns (described in the report for 1951). This study showed that when coarse- and fine-fibered cottons of equal staple length were processed into rovings of equivalent size, the coarse-fibered required more twist than did the fine-fibered cottons.

The efficiency with which cotton fibers are drafted at the spinning frame is largely dependent on the amount of twist inserted in the roving. Now that many mills are routinely determining the fineness of their cottons, use of the new roving twist formula should result in significant increases in processing efficiency and yarn quality.

Partially acetylated cotton produced commercially for its superior heat resistance

Because of its superior heat resistance, some 2 million square yards of partially acetylated cotton cloth is being produced annually for use in pads and covers for laundry presses and home ironing boards. Treated products give from 3 to 6 times the service life of comparable untreated cotton cloth. The future market for these and other acetylated cotton products is estimated at more than 100 million pounds annually.

While partially acetylated cotton is not the first chemically tailored cotton product to be proposed in this country, it is the first to be manufactured on this scale. This development has come at an opportune time to meet competition of the synthetic fibers threatening to displace increasingly large quantities of cotton in the laundry industry, and in other uses where heat, rot, or acid resistance is an important consideration.

The part played by the Southern Regional Research Laboratory in developing this process and the progress steadily made in this research have been described in previous reports. The development was carried from the laboratory to a pilot-plant scale and diverse service tests repeatedly indicated the superior performance of this modified cotton, first in the end uses requiring rot resistance, and later in the heat-resistant products.

Two manufacturers now producing acetylated cotton are using batch processes. They have not had to invest in special machinery, since standard textile equipment requiring relatively little adaptation is satisfactory. Meanwhile, speedier acetylation by a continuous process using machinery designed for the purpose, has been developed in cooperation with the Southern Laboratory by a third manufacturer.

Extensive pilot-plant research at the Southern Laboratory is largely responsible for acceptance of the process by industry. Technical information was provided which helped in translating to full-scale operation without extensive and time-consuming development. Also, considerably simplified methods of chemical analysis and control procedures were worked out to permit reliable and uniform operation of the process without need for highly technical supervision.

New cotton flameproofing treatment under development

As mentioned in the report for 1952, several promising flameproofing treatments for cotton are being investigated at the Southern Regional Research Laboratory in cooperation with the Army Quartermaster Corps. Flameproofing for civilian purposes—in clothing, draperies, upholstery, curtains, bedding, and other household articles—is also of considerable commercial interest.

No completely satisfactory commercial flameproofing and glowproofing treatment had been previously developed. Generally, available flameproofing treatments for cotton either fail to stand up after laundering, or they weaken the fabric or develop other objectionable properties—stiffness, stickiness, and increased weight. Some treatments which are otherwise effective are not suitable for clothing because they are harmful to the skin; are not economical because they use chemicals not readily obtainable; or require adaptation or change of usual finishing equipment.

The Southern Laboratory has developed one new flameproof treatment beyond the test-tube stage. Tetrakis (hydroxymethyl) phosphonium chloride (THPC) is used as the key chemical in the new resin treatment which gives not only durable flameproofness and glowproofness but also wrinkle-resistance and rot- or mildew-resistance. Wrinkle-resistance enhances flameproofed fabrics for use especially in clothing, draperies, and curtains; rot resistance is desirable in cotton materials for tentage, awnings, and the like.

The new treatment meets many other requirements. Treated fabrics retain their flameproofness after numerous launderings, they

have a good hand, and are permeable to water vapor; when a softener is added, tear strength lost during treatment is restored, and tensile breaking strength is not changed.

THPC is a crystalline compound produced by reacting phosphine with formaldehyde and hydrochloric acid. It is made from inexpensive chemicals by a process adaptable to commercial production. The flameproofing finish is made by mixing THPC in water with methylolamine, urea, and triethanolamine, all commercially available. Conventional finishing equipment is used for applying the chemicals, drying, and heat-curing. Fabrics can be treated to obtain any degree of flameproofness desired for a specific use.

Because of the interest shown in this development by commercial cotton processors, at least one firm is making THPC on a pilot-plant scale. Several textile finishing plants are applying the treatment to cotton fabrics to study its feasibility for commercial use and to evaluate further properties of the treated fabrics.

Wool

New laundry detergent additives for minimizing deposition of soil on wool and other fabrics

Under the sponsorship of the Quartermaster Corps, a basic investigation of detergency is being conducted at the Western Regional Research Laboratory to develop improved fabric cleaning procedures for military field use.

One phase of this investigation has been concerned with the mechanism of soil redeposition in laundering, manifested by a gradual dulling of the fabric after repeated washing. This redeposition must be prevented to obtain clean, bright cloth. Little is known about the mechanisms of soil suspension involved in laundering operations. This type of information is so far behind the knowledge of wetting, deterging, emulsifying, foaming, and other properties of surface-active materials that it has become perhaps the limiting factor in improving laundry detergents and laundering operations. This is especially true in the use of synthetic detergents, particularly the anionic type, which in their present state of development are inferior to soap (when used in soft water) in soil-suspending ability.

One of the best answers to the problem of soil redeposition has been the addition of sodium carboxymethylcellulose to detergent products. This additive has found wide acceptance for its ability to minimize soil redeposition during laundering operations, but has some undesirable limitations in solubility and in compatability with certain detergent materials. The mechanism by which this additive functions is not clearly understood, and it remains an important problem in understanding detergent action.

Studies conducted by the Western Regional Research Laboratory have shown that in an aqueous cleaning system containing an alkylarylsulfonate detergent and alkaline builders, several proteins and certain other polymeric materials are as effective as sodium carboxymethylcellulose in preventing the redeposition of carbon black, a commonly used test soil, on both cotton and wool fabrics. Among a group of over ten proteins examined, representing a wide range in chemical composition, gliadin (derived from wheat gluten) appears to be the

most promising. On an equal weight basis, gliadin is superior to sodium carboxymethylcellulose as a soil-suspending additive.

In an extension of this investigation, several selected water-soluble synthetic polymers were studied as model protein compounds. It has been found that the nonionic polymers are, in general, more effective than the ionic types, and that there exists an optimum average molecular size (ranging from about 10,000 to 40,000) of these nonionic polymers for maximum effectiveness as soil-suspending additives. Among the nonionic polymers examined, polyvinylpyrrolidone and partially acetylated polyvinyl alcohol appear to be as effective as sodium carboxymethylcellulose in preventing soil redeposition.

It is anticipated that through further study of these new soil-suspending additives and of the related mechanism of detergency actions, improved cleaning compounds and procedures may be developed.

Comparison of physical properties of wools from different breeds of sheep

While it has long been known that wools produced by different breeds of sheep have characteristic differences, the specific differentiating physical properties have never been completely determined. Such information would be of great value in bringing wool quality standards into closer correlation with commercial requirements and in assisting growers to move more surely toward a general upgrading of their product.

The characteristics by which wool fabrics are evaluated—including drape, softness, loftiness, and wrinkle- and abrasion-resistance—are largely related to the physical properties of the wool fiber as well as of the fabric. These properties also determine the efficiency with which fibers can be spun into yarns and subsequently woven into fabrics.

A cooperative study with the California Agricultural Experiment Station was undertaken by the Western Regional Research Laboratory to compare the physical properties of wools from five breeds of sheep. The breeds were selected so as to furnish representative types of fiber fineness from the entire range of wools produced in this country. Rambouillet (very fine wool), Columbia (medium fine), Suffolk (medium coarse), Lincoln (very coarse and uniform), and Navajo (very coarse and nonuniform) sheep were raised on the same feed and under the same environment. Wool samples studied were taken after one year of growth.

Marked differences in behavior with respect to elasticity, stiffness, and ability to recover from deformation were found to exist between fibers of the different breeds and were related, in part, to the fineness of the wool. For example, wool from the Columbia breed, developed by crossbreeding the fine-wool Rambouillet breed with the coarse-wool Lincoln breed, is intermediate in fineness between the parent breeds, and was found to be intermediate in stress-strain characteristics. Navajo wool, a coarse wool, is similar in stress-strain properties to the coarse Lincoln wool.

The studies also revealed some differences in mechanical properties which are independent of fiber diameter, and which appear to be associated with "crimpiness" (waves or kinks per inch). For instance, Suffolk wool, a medium coarse wool, exhibits stress-strain properties

similar to those of the more-desired, fine-fibered Rambouillet wool. Significantly, both types of wool have comparably high crimpiness. The finer wools are more desired because they spin to finer yarns and yield softer fabrics. These findings substantiate the belief held by some breeders that in addition to fineness and other properties, the degree of crimpiness is an important consideration in characterizing wool as a raw material. Further research will be needed to establish these relationships on a fully quantitative basis.

MEDICINALS

Absorption and metabolism of rutin

The extensive technical information developed by the Eastern Regional Research Laboratory on rutin—a rhamno-glucose of quercetin found in a large number of plants such as buckwheat, asparagus, and tobacco—has paved the way for the use of this substance therapeutically, for certain types of hemorrhagic conditions. For such purposes it has been administered orally.

Some users of rutin have had few or no favorable results, however, and their failures have led to considerable controversy as to the mechanism of rutin absorption and its ultimate metabolic fate. A study of the excretion of the orally administered drug in humans and rats was reported in the August 1950 issue of a medical journal, wherein the authors concluded that rutin is not absorbed from the gastrointestinal tract, but destroyed in the feces. This report, together with the known poor solubility of rutin in water and the failure of some clinicians to obtain beneficial results from rutin therapy, has given rise in some quarters to the opinion that the drug can have no therapeutic value due to lack of absorption in the body.

The explanation of these negative results on absorption lies in the fact that investigators had been searching for rutin excreted in the urine, and interpreting failure to find it as proof of absorption failure. Studies made at the Western Regional Research Laboratory on the absorption, metabolism, and mechanisms by which rutin produces its physiological effects, have produced conclusive evidence that when rutin is given orally to rabbits it is absorbed, and instead of being excreted in the urine as rutin it is metabolized or broken down into a number of compounds of smaller molecular size. One of these metabolites has been isolated from the urine and positively identified as 3,4-dihydroxyphenylacetic acid, which does not occur in normal rabbit urine. The amount of this compound recovered from the urine shows that at least 25 percent of the rutin administered is absorbed. This estimate of the amount of absorption will quite probably increase as investigations in progress result in identification of other metabolites.

This research is significant not only because it tends to confirm the value of the pioneering work on rutin at the Eastern Laboratory, but also because it suggests that the related flavonoids which are found in many food products can be absorbed by the body, in spite of their characteristic low solubility in water, and thereby play a significant role in various physiological processes.

Steroidal cortisone precursors

The search among wild plants for steroidal sapogenins of suitable structure and high concentration has continued at the Eastern Re-

gional Research Laboratory, in cooperation with the Bureau of Plant Industry, Soils, and Agricultural Engineering. During the past year about 800 additional samples have been received, making a total of more than 3,500. Developments in research on these plants are reported herein.

As a result of industry's successful microbiological introduction of oxygen in the key 11 position, starting with progesterone, the search for suitable plant steroids has somewhat narrowed to those which are the most readily converted to progesterone. For this reason diosgenin has become the most attractive plant precursor, and may eventually replace bile acids. Sarsasapogenin and smilagenin would also be of interest.

A number of *Dioscorea* species (Mexican yam) with unusually high diosgenin content—ranging from 4 to 8 percent, moisture free basis—have been found. The latter value is probably the highest on record. As much as 3.0 percent sarsasapogenin, and 2.0 percent smilagenin, also highest values reported, have been found in several *Yucca* and *Agave* species, respectively.

Many *Agave* and *Yucca* species have enzymes which can hydrolytically cleave steroidal saponins to sapogenins. Further research has resulted in the discovery that many common molds can adaptively form similar enzymes when grown on saponin substrates. These discoveries could be of particular value if applied to the aqueous byproducts resulting from manufacture of fiber from *Agave* and *Yucca* leaves. The steroid content of such aqueous liquors is so low that the usual solvent extraction and acid hydrolysis procedures are not practical. However, since sapogenins are water insoluble, they probably can be economically recovered following enzymatic hydrolysis of dilute liquors. Recovery of useful byproducts may encourage production of these hard fibers in the United States.

A number of useful analytical methods have been developed. A complete catalogue of the infrared spectra of sapogenins and their derivatives has been compiled, thereby permitting identification of unknowns by direct comparison of infrared spectra. It has been found that steroidal sapogenins treated with sulfuric acid form chromogens having characteristic ultraviolet spectra. This method can be used both for qualitative detection and quantitative estimation. Detection and identification of microgram quantities of steroidal sapogenins has been accomplished by means of paper chromatography. By utilization of solvent systems such as propylene glycol-cyclohexane and acetic acid-cyclohexane, separation of all common sapogenins has been accomplished.

During the screening of plants for cortisone precursors a new sapogenin was discovered in the leaves of several *Yucca* species. The compound, named markogenin in honor of the pioneering saponin chemist Russel Marker, is a dihydroxy analogue of sarsasapogenin, with which it is invariably associated.

Sapogenins are useful for cortisone synthesis primarily because the 3-step degradation of the sapogenin side chain to the pregnane structure can be accomplished with facility. Conventionally, the last step of this reaction involves saponification at reflux temperatures in methyl or ethyl alcohol. Under these conditions, undesirable byproducts and low yields are always obtained. Research on this key

step has resulted in the finding that use of tertiary butanol at room temperature eliminates byproducts and consequently results in higher yields of pregnane intermediates.

During studies on the suitability of hecogenin as a cortisone precursor, a new reaction of the carbonyl group at position 12 was discovered. It was found that perbenzoic acid under suitable conditions quantitatively converts hecogenin to a 7-membered ring C lactone. This reaction was used to form acids and alcohols in high yields. These latter compounds form a new series of steroids with ring C open. It is possible that these compounds or their hormonal analogues may have some desirable physiological properties.

Qualitative testing of plant extracts for nonsteroid groups of constituents—flavonols, alkaloids, tannins, and unsaturated sterols—has continued. Among the plant samples numbered 1,200 to 2,500, a plus 3 rating was given to 3 species for flavonols, to 14 species for alkaloids, to 99 species for tannins, and to 169 species for sterols. Plus 2 or plus 1 ratings were given to even larger numbers of samples.

After examination of some 100 species of *Dioscorea* from various parts of the world a generalization was reached: Those native to the Western Hemisphere do not contain alkaloids; some from South Africa, Kenya, Sumatra, Philippines, and the Malay Peninsula do. Furthermore, within the materials so far examined, those that contain alkaloids do not contain diosgenin. Abundant alkaloid was found in *Pinus sabiniana*, the first species in which it has been recorded in the Pinaceae, and only the second species in all the gymnosperms.

Tabular data on the first 2,000 samples are available to plant chemists and pharmacognosists who may be interested.

Advances in dextran research

Contributions of the Northern Regional Research Laboratory to production of a synthetic plasma volume expander from dextran were described in the 1952 report. Developments during the past year have demonstrated the value of these contributions in providing the Nation with a readily available product for supplementing the limited available supplies of plasma, not only for military and civilian defense needs but also for normal domestic requirements. Results of field trials by the military in Korea, in addition to large-scale tests of clinical dextran in military hospitals both here and abroad, have led the Army to announce that dextran will be used in large measure in place of blood plasma for all requirements at home and overseas. These tests indicate that dextran is equal to plasma in the prevention and treatment of shock. In addition, an important advantage of dextran is that it does not transmit a virus-type hepatitis (jaundice) as does plasma in a small percentage of cases.

Four companies, using the dextran-producing organism *Leuconostoc mesenteroides* NRRL B–512 and culture methods discovered at the Northern Regional Research Laboratory, are now producing clinical dextran at a yearly rate of 2,560,000 pints of 6-percent solution. Another company is expected to begin production in the near future.

During the past year research on dextran at the Northern Laboratory has led to several notable developments. These concern improved processes for more economical production, and advances in the physical and chemical knowledge of the structure and synthesis. Improvements have been made in analytical and physical methods for the con-

trol of clinical dextran production. These developments are described briefly below.

Pilot-plant production of dextran by culture filtrate process.—In the report for 1952, methods were described for producing culture-filtrate liquors high in dextran-synthesizing activity but free from bacterial cells. Addition of sucrose to these liquors, which need not be kept sterile, has resulted in the formation of high-molecular-weight dextran. Precipitation of the natural dextran followed by sulfuric acid hydrolysis and methanol fractionation produces a dextran suitable for clinical use. During the past year, a 33-percent yield of natural dextran, based on total sugar used, has been obtained in pilot-plant investigations. By hydrolysis and fractionation, 38 to 39 percent of the native dextran is converted to a product which meets clinical specifications. Overall yield of clinical material, therefore, is approximately 13 percent, based on total sugar used.

The culture-filtrate process possesses definite advantages over the whole-culture method. Plant operations are simplified considerably and, as a result, less equipment is needed to produce a given amount of clinical dextran. In addition, a higher yield is obtained by the enzyme process.

Increased yield of clinical dextran by establishment of optimum hydrolysis and fractionation conditions.—In the early stages of the development of dextran for use as a blood volume expander, several different micro-organisms were used commercially. However, superior properties of dextran produced by the organism *Leuconostoc mesenteroides* NRRL B–512 have now prompted its use by all producers in the United States. This dextran, therefore, has received primary attention during the past year at the Northern Laboratory.

The NRRL B–512 dextran as synthesized by the micro-organism has a molecular weight of many millions, while the product needed for preparing clinical injection solutions must have a molecular weight near that of normal blood plasma proteins—about 75,000. Partial hydrolysis of natural dextran with acid and separation by alcohol fractionation of the molecules having desired molecular weights proved to be a convenient and economical process for obtaining dextran with the proper characteristics. The problem then was to devise optimum techniques and procedures for converting as much natural dextran as possible into usable form.

Extensive laboratory study of both the hydrolysis and fractionations steps has resulted in establishment of conditions for isolation of 43 to 57 percent of the original dextran as a fraction of lower molecular weight meeting all current chemical and physiochemical requirements for injection-type dextran. This improved yield is more than double that obtained at the initiation of these systematic studies. Variables investigated in the hydrolysis were kind of acid used, dextran concentration, time, temperature, pH, and extent of hydrolysis. In the fractionation step the temperature dependence of the process and the use of both methyl and ethyl alcohols as selective precipitating agents were studied.

The results of these hydrolysis and fractionation studies have been actively sought by industry and have been freely disseminated as acquired.

Progress made toward direct production of clinical dextran by control of enzymatic polymerization.—All dextran-producing bacteria

which have been investigated, with a single exception, elaborate dextrans having average molecular weights in excess of 6 million. To be acceptable as a plasma extender by the military services, an average molecular weight no greater than 100,000 can be tolerated; furthermore, it is necessary that the range of molecular weights be fairly narrow. Dextrans produced by the whole-culture method, therefore, must be degraded to a smaller molecular size by some process, such as acid hydrolysis, and the fraction having proper molecular weight separated. Cost of hydrolysis and fractionation comprises a large fraction of the production cost prior to bottling, and the saving to be made, if dextran were synthesized directly to the proper molecular weight, is evident.

Progress toward direct production of clinical dextran has been made in laboratory experiments by controlling the conditions of reaction between sucrose and the dextran-synthesizing enzyme system. Methods have been developed for separating the enzyme system, dextransucrase, in high-potency yield from cultures of *L. mesenteroides* NRRL B–512. Three conditions were found to divert the synthetic reaction from high to low molecular weight dextran production: (1) High initial sucrose concentration in the reaction mixture, (2) the presence of certain sugars, such as fructose or maltose, (3) addition of low molecular weight dextran to the reaction mixture. By adding varying amounts of low molecular weight dextran to reaction mixtures in which the fructose concentration is kept low and the ratio of enzyme to sucrose high, it has been possible to produce good yields of dextran having molecular weights in the range of 35,000 to 350,000. Preliminary characterization of some of these dextrans by infrared absorption measurements and periodate oxidation analysis has indicated no structural differences compared to NRRL B–512 dextran prepared by conventional methods. On a semi-pilot-plant scale yields of clinical dextran compare favorably with those produced by the whole-culture method.

Chemical structure of dextrans.—Noteworthy advances have been made at the Northern Laboratory in the study of dextran structure through the application of periodate oxidation, methylation, and partial acid-hydrolysis techniques. This threefold approach provides a firm scientific basis for assigning definite molecular structures to dextrans. Such structural knowledge is important not only for correlation with results of clinical trials but also for studies on the structures of other polysaccharides such as starch and its fractions.

For the study of dextran structure by periodate oxidation, a new procedure has been devised for the isolation in good yield of the intermediate oxidation product in the series of steps involving oxidation, reduction, hydrolysis, and determination of D–glucose, glycerol, and erythritol. Application of the improved procedure to a number of dextrans has shown the presence of fewer 1,4-linkages and more 1,3-linkages than had been indicated by routine analytical periodate procedure.

Methylation analysis of NRRL B–512 dextran, with the assistance of a micromethod newly developed at the Northern Laboratory, confirms the presence of about 5 percent of 1,3-glucosidic linkages built into the molecule at points of branching. These results were substantiated by column chromatography. The procedure for isolation of a

completely methylated dextran in high yield has been improved and applied to a number of other dextrans that will be examined by hydrolysis and chromatography.

For the first time reliable evidence has been obtained on the length of side branches in the molecules of dextran from NRRL B–512, as well as two other dextrans. Our findings have been derived from a comparison of measured and theoretical yields of small fragments obtained when dextran is partially broken down by means of acid. The molecules of the three dextrans apparently all have a comb-like structure involving main chains of 1,6-linked anhydroglucose units to which branches, predominately only one glucose unit in length, are attached. The comb-like structure helps account for the previously unexplained observations that some properties of NRRL B–512 dextran differ from those of the amylopectin fraction of starch which has the same ratio of branch points but a tree-like molecular structure.

New information on properties of dextrans developed by basic physical studies.—Different structural types in dextrans elaborated by different bacteria have been distinguished by differences in solubility, infrared absorption, and optical rotation. The most characteristic difference in infrared patterns of dextrans is the absorption at 12.6 microns. It has been found that increased absorption at this wavelength is paralleled by an increase in optical rotation. Introduction of 1,4-glucosidic linkages would not be expected to affect optical rotation; hence these physical observations indicate the presence of 1,3- or 1,2-linkages in many dextrans in addition to the predominant 1,6-linkage. Chemical evidence has demonstrated that in several dextrans having marked infrared absorption at 12.6 microns, the secondary type of linkage is 1,3. This correlation enables a rapid preliminary survey of structure type to be made by the infrared method.

The heterogeneous character of native, high molecular weight dextrans with respect to size has been demonstrated by ultracentrifugation studies. Further, it has been shown that certain of these dextrans can be separated into fractions which not only differ in molecular weight but also in chemical structure. For at least one dextran, relative amounts of these distinct chemical components vary with culture conditions.

Measurement of molecular dimensions in a series of fractions of acid-degraded NRRL B–512 and NRRL B–742 dextrans has established relations between their dimensions and weights. Data show that size of the NRRL B–512 dextran molecule increases more slowly with molecular weight than would be predicted for a linear unbranched molecule, or for a linear molecule having short branches of uniform length at uniform intervals. Models having more extensive branching are in better agreement with the physical data. Compared to NRRL B–512 dextrans, molecules of NRRL B–742 are more compact, and the dimensions increase less rapidly with molecular weight. More branching is therefore found in NRRL B–742. Quite apart from their structural significance, these size measurements are important to the clinical application of dextran, because it is molecular dimension rather than molecular weight that must determine whether a particular dextran molecule can permeate kidney or vascular membranes.

A series of narrow fractions from hydrolyzed NRRL B-512 dextran, covering the molecular weight range from 15,000 to 1,000,000, was characterized by the ultracentrifugal method. Sedimentation constants for these fractions were correlated with light-scattering molecular weights and other molecular weight averages. Relations thus obtained are being used to analyze polydispersity of clinical dextran preparations.

New dextrans and their characterization.—Dextrans from over a hundred individual strains of bacteria have been prepared, purified, and characterized. This information provides a scientific basis for establishing a relationship between the chemical structure of dextrans and such aspects as suitability for use as a blood volume expander, serological behavior, and value for industrial applications. These findings are also useful in classification of bacteria that produce dextran.

Correlations have been established among these characteristics of dextrans and dextran-producing bacteria and results have permitted classification into significantly different chemical and serological types. Characterization of many typical dextran preparations according to homogeneity of molecular constitution and size has provided evidence of fundamental importance for the study of dextran production and selection of dextrans for particular uses.

This survey has disclosed dextrans which provide rich sources of heretofore unknown or unavailable oligosaccharides composed only of glucose. It has encompassed the most extensive group of polysaccharides ever before studied, and yet all indications are that only a mere beginning has been made in the discovery, study, and application of polysaccharides from microbial and other sources. It is now apparent that starches, dextrans, and other yet undiscovered glucose polymers merge into one continuous series through intermediate types, some of which have been found in this survey.

Analytical methods for determination of dextran and associated carbohydrates.—Basic to control of production and investigation of chemical and physical properties of dextran are analytical methods for its determination. Three methods have been developed for this purpose at the Northern Laboratory. The anthrone method, which is applicable to microgram quantities of dextran, has been improved to give an accuracy of 0.5 percent. More rapid in their application are the polarimetric and the refractometric methods for which the fundamental constants, specific rotation and the refractive index increment, have been determined. The latter have been adopted by commercial producers as control methods.

Since fructose and its polymer, levan, are found as impurities in dextran preparations, two analytical methods have been developed for their detection and measurement. One is based on the reaction with resorcinol in the presence of hydrochloric acid—earlier methods having been modified to reduce the interfering effect of D-glucose to one-third of the previous value. A new method, using an alcoholic anthrone reagent, has the added advantage of requiring such small amounts of material that it can be used in quantitative paper chromatography. In addition, a qualitative procedure has been developed to determine whether the fructose measured in quantitative procedures actually is present in a form of the levan type. This procedure in-

cludes paper chromatographic techniques applicable to other studies involving fructose. Information obtained on some samples by use of these methods indicates that fructose may be a part of some dextran molecules, although the amount probably is less than 1 percent.

Methods have been developed for the quantitative measurement by paper chromatography of amounts of D-glucose, disaccharide, and higher saccharides in mixtures. These methods have proven indispensable in connection with studies of dextran structure, as well as in analysis of byproducts of enzymic synthesis of high molecular weight dextran.

Total acid hydrolysis of polysaccharides is a necessary step in determination of constituent sugar units and is also used in many cases for determination of the amount of polysaccharide in a solution or solid. Optimum conditions have now been established for total hydrolysis of dextran within the practical period of an hour.

Collaborative test of light-scattering method for molecular weight determination initiated.—To meet military specifications the molecular weight of clinical dextran, as determined by light scattering, must fall within prescribed narrow limits. All producers, as well as the Armed Services Medical Procurement Agency, therefore, use this method to measure molecular weight, and it is important that its precision as a routine control procedure be established. For this purpose, the Northern Laboratory has initiated a collaborative test in which all domestic producers and interested Government agencies are cooperating. Multiple samples of three dextrans of different molecular weight are being analyzed according to a statistically designed experiment which will give maximum information on the precision of the method.

Cooperation.—Numerous medical and other research groups have been provided with highly purified natural dextrans and dextran fractions having wide variations in chemical structure, and with the rare sugars—isomaltose and isomaltotriose—produced at the Northern Laboratory from NRRL B–512 dextran. These substances have been used in serological, immunological, biochemical, and allergenic investigations related to safe and successful use of clinical dextran. These investigations have been carried out in the Allergen Research Division of this Bureau and at the following medical colleges or centers: Cornell, Columbia Presbyterian Hospital, Emory, Pittsburgh, and Walter Reed. Never before have such highly purified and well-characterized substances been available for fundamental investigations. The significance of results already obtained extend beyond the problems concerning clinical dextran and its use into previously inaccessible regions of fundamental progress. Some of the problems involve relationships between antigen structure and serological behavior, structural and spatial groupings in antigens and antibodies, protein-carbohydrate interactions, and cross-reactions between pathogenic and nonpathogenic bacteria.

Cultures of the dextran-producing organism *L. mesenteroides* NRRL B–512 have been furnished to research groups of 49 companies and universities in this country and to 31 groups abroad. Requests for this organism have demonstrated the world-wide interest in dextran as a plasma volume extender and recognition of the superior properties of dextran produced by strain NRRL B–512.

Starch sponge for use in controlling bleeding, commercially available

Several years of clinical evaluation of starch sponge as an agent to control bleeding have given such satisfactory evidence of the safety and usefulness of the sponge for this purpose that one company has obtained clearance of its product by the Food and Drug Administration and is now producing it commercially. The starch sponge is manufactured in the form of blocks, powder, dental cones, and cones for special surgical operations. Commercial interests in other allied therapeutic applications is reported.

The sponge is a physical form of starch obtained by freezing and thawing a starch paste or gel. Fundamental studies of the changes involved were made some years ago at the Northern Regional Research Laboratory. During the course of the work it was found that the sponge is solubilized by action of enzymes in the animal body. Thus, in some surgical applications, there is no need to remove the sponge; it is converted into sugars which are absorbed by the body. Water-insoluble materials that are added to the paste before freezing become an integral part of the sponge. It was therefore suggested by the Northern Laboratory that starch sponge might be useful in surgery to carry medicaments, such as antibiotics, for slow release in the body as the sponge is solubilized by body enzymes.

A nationally known obstetrician and gynecologist made animal and, later, clinical experiments with starch sponge and discovered its hemostatic property. He has published three papers in prominent medical journals on results in over 100 clinical cases. Papers have also been published on the clinical use of the sponge in prostate gland operations, in dental surgery, and on the mechanism by which it acts to control bleeding.

The Laboratory has developed methods for making sponge of the desired texture and for sterilization of the product. For both animal and clinical experimental studies it has supplied several hundred pounds of the sponge in block and powder form to the Departments of the Army and Navy, Veterans' Administration, civilian hospitals, and members of the medical profession. Industrial firms interested in possible commercial production have also been supplied. Several firms have sent representatives to the Laboratory to study the method developed there for preparing the surgical sponge, and to discuss conversion of the method to an industrial scale.

Starch sponge presents an excellent example of the development of an entirely new industrial product on the basis of information obtained from fundamental study of an established agricultural product.

Cinnamycin—a new antibiotic

A search has been conducted by the Northern Regional Research Laboratory for antibiotic-producing micro-organisms whose metabolic products adversely affect the growth of strict anaerobes, such as *Clostridium botulinum*, or acid-fast micro-organisms such as *Mycobacterium tuberculosis*. A *Streptomyces* isolate from a sample of Japanese soil was found to inhibit the growth of various gram-positive rods but had little effect on gram-positive cocci. Since this type of activity had not been previously encountered, further detailed studies were made on this *Streptomyces* culture. Following physiological

and morphological studies, the culture was assigned a new species name, *Streptomyces cinnamoneus*, NRRL B–1285.

A suitable culture medium was developed for producing the new antibiotic, cinnamycin, from NRRL B–1285. It was isolated by ion-exchange chromatography, and purified by alumina chromatography and then by Craig countercurrent distribution.

Chemical studies showed cinnamycin to be a polypeptidic antibiotic containing arginine, aspartic acid, glutamic acid, pretine, phenylalanine, valine, lanthionine, β-methyllanthionine, and, possibly, cystathionine or *allo*-cystathionine. Thus, it is similar to other polypeptidic antibiotics in that it contains residues not commonly encountered in proteins. Cinnamycin is unusual in that it contains three sulfur-containing amino acids and is, possibly, the first example of an antibiotic containing cystathionine or *allo*-cystathionine. Among the actinomycete polypeptidic antibiotics, it is the first found to have such amino acids.

Cinnamycin is stable and can be stored under refrigeration for months in the dry state or in aqueous solution in the cold without apparent loss of activity. In solution, it is not inactivated by boiling in the pH range 2–9, or by pepsin, trypsin, or light.

Antagonism of cinnamycin is limited to certain gram-positive rods and *Mycobacterium* species. It is active *in vitro* at 5 μg./ml. against streptomycin-resistant *M. tuberculosis* and at 1 μg/ml. against *Cl. botulinum*. While its consideration as a therapeutic agent in tuberculosis is probably ruled out by its toxicity (LD_{50}=12 mg./kg. in mice, intraperitoneally), it may prove useful against *Cl. botulinum* in food and against local clostridial infections.

INDUSTRIAL PRODUCTS

Animal fats in industrial tin plating

Cooperative research of scientists at the Eastern Regional Research Laboratory and the Armour Research Foundation has shown that our better grades of domestic tallows and greases, suitably processed, are fully as satisfactory as imported palm oil in the hot dip tinning of steel sheets for can manufacture.

The processing required for making tallows and greases suitable for tinning is similar to that used in making shortenings, and involves refining, partial hydrogenation, and deodorization. The free fatty acid content is adjusted to about 8 percent, and the product stabilized with 0.05 percent of a suitable antioxidant.

A full scale plant test of experimental animal fat in the industrial hot dip tinning process has now been completed. Results show that it is equal to palm oil in every respect. About 15,000,000 pounds of palm oil are now being imported annually for tinning. Therefore, the research not only opens a market for sizable quantities of our surplus domestic fats but also relieves one of our important industries of its present complete dependence upon an imported product.

Epoxidized fats in vinyl plastics

Some 500 million pounds of the approximately 2 billion pounds of synthetic resins produced in the United States annually are vinyl chloride resins. These vinyl resins require the addition of about 150 to 200 million pounds of plasticizers, usually prepared from coal

tar and petroleum derivatives, to render them flexible and soft enough for most uses.

Fats have several properties that make them desirable for use as plasticizers but are generally not compatible with vinyl chloride resins. However, by reaction of fats and fatty esters with organic peracids, such as peracetic acid, research workers at the Eastern Regional Research Laboratory were able to convert unsaturated fatty materials to a form which was compatible with these resins. These modified fats, called epoxidized fats or epoxidized fatty esters, have the valuable property of stabilizing vinyl chloride resins, thereby substantially increasing the useful life of the finished product and permitting these resins to be used in applications where they are exposed to heat and light. This stabilizing effect is a consequence of the avidity with which epoxidized fatty materials neutralize hydrogen chloride which is liberated when the vinyl chloride resins decompose. Free hydrogen chloride accelerates further decomposition with subsequent embrittlement, discoloration and, finally, deterioration of the plastic.

Epoxidized fatty materials, especially epoxidized soybean oil, are being used in large quantities by industry but actual production figures are not yet available. Six industrial concerns have been licensed to operate under patents assigned to the Secretary of Agriculture.

Canaigre semiworks plant producing tanning extract

A semiworks plant for producing tanning extract from dried canaigre roots has been set up at the Eastern Regional Research Laboratory. From 2-year-old cultivated roots, more than a ton of dried canaigre extract has been produced for evaluation in commercial plant tanning tests. Each test will require 5 to 10 tons of dried extract. These cultivated roots require a somewhat different extraction procedure than that for the older wild roots used for design of the plant; however, it is evident that the same basic process can be used. Although the most desirable operating conditions have not been entirely resolved, the plant is now producing tanning extract of a quality similar to that previously extracted in the pilot plant from wild roots and used to produce the leather recently tested in shoe soles.

Canaigre tannin makes serviceable sole leather

A shoe service test has demonstrated that leather soles tanned with a blend containing an extract made from canaigre roots—cultivated from a plant now growing wild in the southwestern United States—wear as well as leather soles tanned with a commercial tanning blend. In addition, the canaigre tanned leathers were equal in color, thickness, and weight.

The sole leathers used were made from 16 double bends (cattle hides with heads, shoulders, and bellies removed) cut into right and left single bends. The 16 left bends were tanned at the Eastern Regional Research Laboratory with a vegetable tanning blend, the tannin content of which consisted of 50 percent canaigre and 25 percent each of quebracho and chestnut. The 16 right bends from the same hides were tanned at a tannery, using a regular commercial tanning blend. Its tannin content consisted of 30 percent quebracho, 20 percent chestnut and 50 percent of other commonly used tannins. After tannage, both lots of leather were extracted, bleached, oiled, and finished by the same procedure. Average leather yields calculated from white

weights (weight of wet, unhaired, fleshed hide before going to the tanning liquors) and the finished leather weights were, for the canaigre leather 73.3 percent, and for the commercial leather 70.7 percent. In thickness the average values were, for the canaigre leather 8.8 irons (an iron is 1/48 inch), and for the commercial leather 8.5 irons. Of the two leathers the canaigre leather was a little lighter in color, otherwise there appeared to be no important difference.

For the service test, seventy pairs of garrison type shoes were made in the sizes required by the postmen who participated. To avoid quality differences due to hide location, each pair of outsoles made was cut from corresponding positions on the right and left bends from the same hide, and provision was made to place half of the canaigre leathers on right shoes and half on left shoes. When the first set of soles was worn thin or through, the shoes were half-soled with the same types of leather but with canaigre leather on the opposite foot.

The results of this shoe service test showed that, of the 127 pairs of soles on which the test was completed, soles tanned with the canaigre blend were better than the control soles in 31 cases, equal to control soles in 70 cases, and poorer in 26 cases. Calculated on the basis of the percentage of original leather thickness worn away, the average percent loss of canaigre leather by wear was 81.1 percent and that of the control 82.5 percent.

Cooperating with the Bureau of Plant Industry, Soils, and Agricultural Engineering in their agronomic development studies of canaigre, 84 samples of canaigre roots have been tested for tannin. Seventy-six of these samples showed tannin ranging between 20.5 percent and 41.1 percent. In fertilization studies using 16–20–0 fertilizer at the rates of 100, 200, and 400 lbs. per acre, the roots produced showed tannin contents of 31.26, 31.73, and 31.47 percent (moisture-free basis), respectively, as compared with 30.85 percent for roots from unfertilized control areas.

Approximately 80 tons of shredded air-dried canaigre roots are now available for processing into tanning extract at the Eastern Laboratory semiworks plant. It is proposed to use the extract for semicommercial tanning tests.

Optimum conditions determined for refining soybean oil

Pilot-plant studies of conditions for refining soybean oil to obtain the maximum stability were conducted at the Northern Regional Research Laboratory. Three lots of degummed soybean oil and one of nondegummed soybean oil, both obtained from commercial producers, were used. Refining, bleaching, and deodorization treatments for each batch were as nearly equal as possible except for the strength and amount of caustic used for refining. Iron content and color were determined on samples of refined, bleached, and deodorized oils, and phosphorus, tocopherol and stability by the Active Oxygen Method determined on the deodorized oils alone. Flavor stability data were obtained for the deodorized oils from refining tests with one lot of degummed oil and found to agree with the oxidative stability tests.

Degummed oils were refined with two strengths of caustic, 8° and 30° Baumé, using 0.05, 0.1, and 0.2 percent excess caustic at each strength. The nondegummed oil was refined with 8°, 14°, 20°, and 300° Baumé caustic using 0.05, 0.1, 0.2, and 0.3 percent excess caustic

at each strength. The excess caustic was calculated on the weight of oil in each case.

The most stable oil was obtained from a degummed oil containing 104 parts per million of phosphorus when refined with 0.05 percent excess of 30° Baumé caustic. A degummed oil containing 111 parts per million of phosphorus produced the most stable oil when refined with 0.2 percent excess of 30° Baumé caustic, while a degummed oil containing 270 parts per million of phosphorus gave the most stable oil when refined with 0.05 or 0.1 percent excess of 8° Baumé caustic. The crude nondegummed oil contained 880 parts per million of phosphorus and gave the most stable oil when refined with 0.05 or 0.1 percent of 8° Baumé caustic.

Refining tests were repeated with two lots of degummed oil, and 0.01 percent of citric acid was added before the deodorization step. Citric acid improved the stability in every case; however, the refining condition which gave the most stable oil when the acid was not used also produced the most stable oil when it was used. Tests were also repeated with one lot of degummed oil bleached with 2 percent bleach instead of 1 percent. The optimum refining condition was the same.

Refining conditions had no effect on the color of oil, which was obtained from the crude oil containing the least amount of phosphorus. However, weak caustic produced an oil of lower color than strong caustic in every other instance.

Results indicate that with respect to the color and stability of refined oil, it is preferable to refine a crude, nondegummed or a partially degummed soybean oil by using a small excess of dilute caustic. In two cases, oils that were well degummed gave the most stable oil when refined with strong caustic.

Alcohol and feeds produced from flood-damaged and field-germinated wheat

During the Kansas City flood in June 1951, millions of bushels of grain, mostly Government-owned wheat, were severely damaged. Most of the grain was submerged in the flood waters for 12 days and an additional 2 weeks was required before the first grain could be removed from flooded locations. The only means of salvaging this damaged wheat was by converting it to grain alcohol and recovering the spent grain as distiller's dried feed. In addition to the problem of transporting the moist, putrified wheat to the plants, some distillers reported difficulties in mashing and fermenting the damaged wheat.

Since flood disasters occur periodically and the problem of salvaging flood-damaged wheat will surely occur in the future, production of alcohol from this material was studied by the Northern Regional Research Laboratory. When received, the damaged wheat had been stored in the open for 3 months, was putrid, sour, and hot and had a moisture content of 45 percent. To arrest any further putrification the lot was sun-dried for 1 day, thereby decreasing the moisture content to 12.3 percent.

In a series of laboratory fermentation experiments, an average alcohol yield of 4.8 proof-gallons per bushel was obtained, using 10 percent of barley malt as converting agent and basing the yield on a moisture content of 12.3 percent. This yield can be considered quite satisfactory because the alcohol yield of sound wheat amounts to about 5.0 proof-gallons per bushel under optimal practical conditions.

Observations made during these experiments indicate that during the 3 months of deterioration only a small amount of the original starch was destroyed. The starch content on a dry basis was 68.4 percent—the same magnitude as for sound wheat. The protein content of the damaged wheat, however, was approximately 30 percent below that of sound wheat. Evidently, primarily proteins are destroyed during the spoiling process.

Unfavorable weather conditions during the harvesting season can cause germination of large quantities of wheat in the fields. When harvested, this type of wheat is only of sample grade and must be sold at reduced prices as poultry feed. A better use of field-germinated wheat is to employ it as raw material for production of grain alcohol and byproduct feed.

Wheat, or any cereal grain, when germinated, loses some of its starch content, but its amylase content increases considerably. In the case of wheat, this is especially true. Based on this phenomenon, a mashing procedure was developed whereby starch of field-germinated wheat was converted to fermentable sugars by means of self-contained wheat amylases, without use of barley malt as a starch-converting agent.

Samples of wheat, from the 1951 crop, which contained 20 to 25 percent germinated kernels were obtained from country elevators. The ground samples were mixed with water and heated for 1 hour at 128° F. During this period the pH was adjusted to 5.2. Following the 1-hour holding period at 128° F., the temperature of the mash was increased to 145° F. and again held for 1 hour. Finally, the temperature was raised to 155° F. for 5 minutes in order to sterilize the mash. It was then cooled to the setting temperature, inoculated with seed yeast, and fermented in the customary manner. The alcohol yields obtained with this simple method, adaptable to any commercial grain distillery procedure, indicated a complete conversion of the starch to alcohol. Yields ranged from 4.8 to 5.3 proof-gallons per bushel (56 pounds, dry basis) of germinated wheat. Variation in yield was in accordance with starch content which ranged from 59 to 62 percent on a dry basis. Dried grain residues from these fermentations had the normal composition of wheat distiller's dried grains.

Plasticizers derived from furfural show promise for low-temperature applications

Under a research contract supervised by the Northern Regional Research Laboratory, evaluation studies recently conducted on a group of esters of mono-, di-, and trihydroxy-compounds prepared from furfural derivatives show they have very good properties as plasticizers for vinyl resins. Polyvinyl chloride films prepared with the use of these plasticizers had outstanding low-temperature flexibility. Of 15 esters tested, all but 3 passed a standard flexibility test at –70° F. Several gave films having better physical properties than comparable film using a standard commercial plasticizer. All esters tested were satisfactorily compatible over a wide range of plasticizer concentrations.

Because of their outstanding low-temperature properties, six of these esters are to be subjected to further evaluation tests to determine their behavior in the –70° to –100° F. range. Their excellent solvent properties indicate that they might also have value as softeners for

synthetic rubbers, such as Buna-N, and for other polymers, such as nylon, which are used for production of molded articles.

All intermediates required for preparation of these new plasticizers can be made from readily available raw materials. The condensation products of furfural with acetaldehyde and with acetone are converted to the desired hydroxy-compounds by catalytic hydrogenation. Acids used for the ester preparations are commercially available monobasic, aliphatic acids in the C_4 to C_{10} range.

Sugarcane bagasse demonstrated to be excellent for manufacture of shipping containers

A succession of investigations, beginning in the Northern Regional Research Laboratory and concluding with commercial shipping tests of fiber containers manufactured on a semicommercial scale, has demonstrated that bagasse, depithed and pulped by our laboratory processes, is a very acceptable material for use in the manufacture of shipping containers. This program was carried out with the cooperation of industry, notably Hawaiian and Florida sugar manufacturers and a large number of equipment manufacturers. Other cooperating organizations were the Forest Products Laboratory of the U. S. Department of Agriculture Forest Service; the New York State College of Forestry, Syracuse, New York; and a beverage company which evaluated the containers in commercial shipments.

Laboratory and small-scale pilot-plant tests consisted of the analysis and pulping evaluation of a number of varieties of bagasse from Florida and Hawaii. Practical methods for separating bagasse into fiber and pith and for converting the fiber into pulp were developed on a pilot-plant scale.

These two methods were then tried on a semicommercial scale, using facilities of several cooperating agencies. Both depithed and whole bagasse from Florida and Hawaii were pulped in an 8-foot hydrapulper. Such hydrapulpers were also used in depithing whole bagasse to produce the pith-free fiber. Corrugating medium was manufactured from 1-ton lots of these pulps blended with 15 percent waste corrugating, using a paper machine 40 inches wide. As a control, a run was made using commercial semichemical hardwood corrugating pulp. Physical tests showed the bagasse boards to be of uniformly higher strength, particularly resistance to crushing, than either board made on the same machine from semichemical pulp or commercial corrugating board.

Paper machine runs were also made to produce liner board from blends of bagasse pulp and commercial softwood kraft plup. A control run was made using 100 percent of the kraft pulp. Physical tests showed that liner board from 25 percent bagasse and 75 percent kraft compared favorably with 100-percent kraft board. The 50/50 blend tested slightly below specifications required in the United States but would be acceptable in many other countries.

For end-use tests, three types of beverage shipping containers totaling more than 10,000 boxes were manufactured in a commercial box plant from 23 different combinations of container board. These boxes were subjected to special compression tests by the Forest Products Laboratory and to a complete series of use tests, e. g., drum, drop, and compression, by a commercial container testing laboratory. All

of these tests proved the very high quality of the corrugating medium made from bagasse. In addition, beverages both in glass bottles and in cans were packed in these containers and shipped by railroad with similar merchandise packed in regular containers. Results were entirely satisfactory.

This development demonstrates that the new mechano-chemical process of pulping bagasse and straw is ready for industrial application in the manufacture of high-grade board pulps. The process has been in industrial use for some time by the "Union Mill," Oude-Pekela, Netherlands, in producing high-grade board from cereal straws.

Alcohol-water injection tests on engines operating on low-octane gasoline at low temperatures

Low-temperature operation of motor vehicles with alcohol-water injection is an important problem that must be considered in the efficient use of injection for boosting the octane number of gasoline. Low temperatures are particularly hard on engine operation since they introduce factors such as starting and warm-up difficulties, sludging, and increased engine wear.

A preliminary investigation of this problem was undertaken by the Corps of Engineers at Fort Belvoir, Va., under an agreement with the Northern Regional Research Laboratory. Four commercial engines, two with and two without alcohol-water injectors, were operated in the low-temperature laboratory at temperatures from 0° to −40° F. under an operating cycle which simulated adverse conditions of winter driving most likely to be encountered in house-to-house delivery service, driving to work, to town, and general farm tractor work. Results of these tests showed that, under these conditions, alcohol-water injection resulted in less wear than normal on cylinders, main bearings, and rings, but in slightly more wear on connecting rod bearings. The injection had no effect on performance characteristics, corrosion of internal parts, cylinder head deposits, and lubricant sludging.

BASIC INVESTIGATIONS

Cereal and Forage Crops

Biologically-active substances in alfalfa

Alfalfa, like other green plants, contains a large number of distinct chemical compounds, many of which are important in the health, growth, and general nutrition of animals which consume them. The roles played by some of these compounds, such as carbohydrates, proteins, and the known vitamins, are fairly well understood. However, there are many substances in alfalfa whose chemical nature and physiological importance have not been established. Research on preservation of the nutritive values of alfalfa, as reported by the Bureau in 1950, pointed to the need for more knowledge of these little known materials. Substantial progress has now been made toward their isolation and identification.

Recent studies at the Western Regional Research Laboratory have shown that alfalfa contains at least two different saponins. One has been hydrolyzed to yield a sapogenin which was isolated in pure crys-

talline form and is now under additional study to determine its chemical nature. The other saponin has not yet been separated.

A method has been developed to measure the total amount of saponins present in alfalfa. Determinations made have shown the material to be present in amounts ranging from 0.2 to 1.0 percent of the dry weight of the alfalfa. Studies are being carried out to determine whether factors such as variety, maturity, or season of cutting have any bearing on amount of saponin present. The significance of this possibility lies in the correlation between the saponin content of various alfalfa samples and the degree of chick growth inhibition when these samples are incorporated in the feed. Samples of saponin have been submitted to the Bureau of Animal Industry for further evaluation.

Another of the little-known components of alfalfa is a flavone called tricin, which adversely affects the reaction response of smooth muscle tissue. Some of the tricin fraction has been isolated from alfalfa and purified, and is now being studied for substantiation of the British speculation that it may play some part in bloat symptomology in cattle. Yields of tricin have not exceeded 0.02 percent of the total dry weight of the plant.

Eight different xanthophyll pigments have been isolated from alfalfa. In poultry feeds these yellow plant pigments furnish coloring for feathers, skin, fat, and egg yolk. Additional investigations will be required before positive identification of each compound can be completed.

By use of newly developed methods, organic acids have been shown to make up about 9 percent of the dry alfalfa plant. Ten organic acids have been tentatively identified and others are known to be present.

When information on these little-known constituents is available, plant physiologists will be better able to understand the complex biochemical changes that occur and to determine whether variations in quantity of a constituent are genetically controlled. This knowledge will increase the possibility of breeding or selecting forage plants of higher nutritive value, thus ultimately resulting in improved formulation of feeds containing alfalfa.

Specific soluble wheat-flour proteins investigated for effects on baking characteristics

Wheat flours differ widely in their baking qualities, and these qualities in general depend on the wheat proteins. However, the specific proteins or their properties essential to good baking have not been known. Consequently, in the development of new varieties of wheat or in the blending and milling of varieties now grown, it has been necessary to make actual baking tests to determine baking properties. Quick, reliable tests for evaluating and predicting baking characteristics and applicable to a small quantity of grain, also would speed the progress of breeding programs. As an extension of the coordinated wheat research program reported by the Bureau in 1951, a systematic investigation of the components responsible for variations in baking properties has been undertaken at the Western Regional Research Laboratory.

Recently a physical-chemical method has been adapted to show that differences occur in the albumins (water-soluble proteins) separated

from various flours. In an earlier phase of the investigation, the albumins were found to modify markedly the bread baking behavior of doughs. A relationship between these observations would provide a basis for development of accurate, routine tests of certain baking characteristics of flours.

To evaluate such possibilities, the flours have been separated into gluten, starch, and "solubles" fractions. When these fractions are recombined into doughs, bread equivalent to that made from the original flour is obtained. When "solubles" from other flours are added, those from good quality flours generally improve baking behavior more than those from poor flours.

Another step in the evaluation has been to separate the flour "solubles" into a few groups having constituents of similar characteristics. Of these, the water-soluble proteins (albumins) exert the most marked effect on baking properties.

More detailed studies of albumins are now in effect. Chemical analysis of flour extracts for certain amino acids has been found to be a satisfactory means of estimating the total albumin content. The physical-chemical method has shown, however, the presence of at least 11 different proteins in the total flour albumin, of which 5 occur in appreciable amounts. Albumin preparations from different flours are being examined to determine whether a relation can be shown between the kinds and amounts of individual components and the baking properties of the respective flours.

Information on structure of corn kernel provided corn handlers and processors

In response to frequent requests for information, the Northern Regional Research Laboratory has published results of a detailed microscopic study of the structure of the mature dent corn kernel. Information in the literature was compiled and combined with results of the laboratory's research in a series of four articles.

The significance of structure to corn handlers and processors was pointed out. For example, the hull, endosperm, and germ were shown to be structurally separate parts, a fact which makes possible the dehulling and degermination processes practiced in the dry milling of corn for production of grits and flour, and in the wet milling of the grain for starch production. The outer portion of the hull was shown to be relatively impervious to liquids, but many intercellular spaces were found in the inner layers. These layers are continuous, with similar sponge-like tissues in the tip cap. Water lost from the kernel during drying, or entering the kernel during tempering for dry milling or steeping for wet milling, can pass most rapidly through these intercellular spaces. It is also in the inner hull layers that molds, if present inside the kernels, are often found.

The seed coat, which is the innermost part of the hull, is a thin, noncellular membrane which was shown to be continuous with the hilar layer that is visible as a dark area at the base of the kernel just under the tip cap. The seed coat is permeable to some chemicals but not to others. This fact is of importance in choosing steeping agents or chemicals for other treatments of the kernel.

It was demonstrated that the endosperm cells are filled with starch granules which lie embedded in a proteinaceous matrix that fills each

cell. The matrix must be softened or dispersed to free the starch granules; this is accomplished by the steeping process employed in wet milling. Choice of a steeping agent to obtain greater efficiency in the separation of pure starch must be based upon the starch-protein relationship in the endosperm cells.

A layer of amorphous material was found to lie between the endosperm and germ and to act as a cementing substance between the two parts. Recovery of a high yield of corn oil of good quality is an essential part of both wet- and dry-milling processes. To obtain this end, germ separation must be carried out and a clean separation of germ from endosperm depends upon weakening the cementing layer.

Numerous requests for reprints of the four articles, for illustrated talks on the subject before groups of grain handlers and corn processors, and for popular summaries of the material for trade journals, as well as comments from individual grain handlers and processors, indicate that the work fulfilled an acute and well-recognized need. This is an example of a type of fundamental study which provides information basic to improved methods for handling and utilizing a major agricultural commodity.

Cotton

Measurement of nonfreezing water in cotton fiber—a guide to quality

New fundamental knowledge important to an understanding of the physical behavior of cotton fibers and fabrics has been obtained as a basis for development of new and improved products. Illustrative of this type of exploratory research is an investigation of the nonfreezing water capacities of cotton. When cotton fibers containing moisture are cooled below freezing, all water in the cellulose will not freeze, even at very low temperatures.

Quantitative investigation of this phenomenon presents a new approach to study of the cellulose-water relationship. This relationship is of fundamental importance in a wide variety of cotton textile problems since the physical properties and behavior of fibers are very sensitive to changes in moisture content. Calorimetric data show that the nonfreezing water capacity is increased if cotton is subjected to treatments, such as mercerization, which lead to greater or more rapid penetrability to dyes and finishing agents, higher moisture adsorption, and higher rates of chemical reactivity. Thus, determination of the nonfreezing water capacities of cotton is a guide to the enhancement of those properties associated with greater available surface area.

New and improved instruments permit speedier and more precise measurements of cotton fiber properties

Interest on the part of the cotton industry in development and use of new and improved instruments for measuring the properties of cotton fiber with greater speed and precision is growing. Precise knowledge of fiber properties aids manufacture by allowing the sorting of bales to give even-running lots which process better and result in cotton products of improved quality. Fiber measurements also aid in obtaining cottons best suited to specific end-uses. Mechanization of the Fibrograph which measures fiber length, and the development of a new instrument which measures both strength and

elongation were advances made during the year in this field of research at the Southern Regional Research Laboratory.

A simple method, based on the use of a servo system and a small low-speed motor, has been developed to make the Fibrograph automatic in drawing the curve, or fibrogram, from which the upper half mean length of the cotton specimen is read. With the modified instrument a smoother curve is obtained and the time required to make a series of tests reduced about 40 percent. No basic change in the Fibrograph is required to convert it to automatic operation. The new parts required are standard and commercially available.

A new tester known as the Stelometer—which measures both the strength and elongation of bundles of fibers—was developed in research at the University of Tennessee under a contract project supported by the United States Department of Agriculture and supervised by the Southern Regional Research Laboratory.

This new instrument permits the rapid measurement of fiber elongation (magnified 20–40 times) the first time that a measurement of this potentially important fiber property has been practicable. The loading rate is controlled at a uniform speed, and accuracy is guaranteed since the indicating pointers, themselves almost free of inertia, follow the load and elongation and break their contact with the pendulum when the bundle is ruptured. A method of preparing the fiber bundle for testing without hand contact of the fibers eliminates variations in moisture content of the sample and the attendant strength variations. Jaw pressure on the fibers is controlled by a torque-indicating pointer which is part of the vise used to tighten the jaws.

Another feature of the Stelometer is that determinations can be made when the jaws are separated by selectable distances which can be altered from zero to 7 mm. For several years there has been controversy, based on limited experiments, as to whether zero or greater-than-zero jaw spacing gives a better correlation between fiber strength and yarn strength. This instrument can be easily adjusted to use any jaw-spacing which gives the best correlation.

Uniformity of instrumental measurements of physical properties of cotton fibers determined by check tests

All branches of the cotton textile industry are making increased use of instruments designed to evaluate the physical properties of cotton, commonly called "character." This has increased the need of attaining a uniform level of testing these properties of length, strength, and fineness within a laboratory and between laboratories. To obtain information on the uniformity with which results are being obtained in textile laboratories throughout the country by use of the Fibrograph (to measure the average length and the length uniformity of cotton fibers), the Pressley Tester (to measure strength) and the Micronaire (to measure fineness), a program of interlaboratory check sample testing was conducted during 1951 and 1952 by a Task Group appointed by Committee D–13 of the American Society for Testing Materials. A representative of this Bureau served as Chairman of the Task Group and the Southern Regional Research Laboratory participated in the program as one of the laboratories performing the tests. This Laboratory also handled the preparation and distribution of samples.

Samples from 9 lots of cotton, each blended by use of textile mill equipment to provide 14 stock lots of well-mixed samples, were distributed to 78 laboratories in 1951 and to 142 laboratories in 1952. Participants in 1951 were asked to perform the tests according to regular procedures in use in their laboratories. In 1952 they were asked to check all balances with standard weights and to use either specific methods of the American Society for Testing Materials, or those given by the manufacturers of the testing instruments.

Statistical analysis of the results, indicated the need for more extensive use of one specific method of test for each of the instruments mentioned. The analyses established the value of using standardized samples to maintain uniform levels of testing within and between laboratories and the need of determining practical tolerances for deviations in test results.

Cotton's primary wall—nature and behavior in chemical finishing

The behavior of individual cotton fibers in the manufacture and chemical finishing of cotton fabrics is influenced by the nature of its primary wall—the thin, outer membrane which covers its entire surface. As the surface which comes into immediate contact with processing environments, the primary wall is significantly involved in frictional effects, wetting, dyeing, and similar phenomena.

A technique perfected at the Southern Regional Research Laboratory to loosen and strip the primary wall from the rest of the fiber was described in the report for 1952. The chemical composition and microscopical structure of specimens isolated by this method were also reported. This year additional observations with the electron microscope have revealed that the cellulose fibrils which constitute the woven network of the primary wall are each less than one-millionth of an inch in diameter and are arranged in two systems, the outer parallel and the inner transverse to the length of the fiber. Noncellulosic substances, consisting of a mixture of waxy, pectic, and proteinaceous materials, are intimately distributed throughout this cellulosic fibrillar network.

This knowledge is being applied in an investigation of the effect of chemical finishing treatments typical of commercial practice. Study of the exact role of the primary wall in these operations has not previously been possible. One objective of chemical purification of cotton is to remove the noncellulosic constituents of the primary wall. These substances, when not removed, modify dyeing properties, rate of reaction, and wettability of fiber, since the reagents involved must pass through the primary wall to reach the body of the fiber.

Observations were made with the light and electron miscroscopes on the appearance and structure of the isolated primary wall before and after kiering, bleaching, and mercerization. It was observed that kiering and bleaching removed and noncellulosic substances present in this portion of the fiber but did not disturb or destroy the cellulose to a significant extent. This observation is contrary to the current conception of the effect of kiering and bleaching. The extent of kiering was progressive with time, and within the range of concentration of alkali commercially used seemed to be governed to a greater degree by length of treatment than by concentration.

The work showed that mercerization apparently removes little of the noncellulosic material of the primary wall, but the extent of shrinkage of the primary wall in both lengthwise and transverse directions during mercerization depends on whether the noncellulosic matter has been removed. In the untreated primary wall, lengthwise shrinkage was 3 percent and transverse shrinkage 32 percent; in the purified wall, the lengthwise value increased to 41 percent and the transverse to 58 percent. These observations reveal the restrictive action of the primary wall and give insight into changes in shape and cross-sectional area of cotton fibers as a result of mercerization.

Universal theory of flameproofing cotton developed

It is recognized that basic information to permit an understanding of the mechanism of flameproofing cotton products, and the fundamental differences in effectiveness of various flameproofing techniques is the only sound approach to the development of more effective treatments. Various theories have been proposed to account for the action of different flameproofers, but none proves applicable to all agents for cellulose, as revealed in an appraisal of these theories by chemists of the Southern Laboratory. Described here is a universal theory offered by these workers to explain the flameproofing effect regardless of the agent used, and based on the fact that a single type of chemical mechanism appears to apply in all cases of flameproofing of cellulose.

Cotton burns after exposure to a flame because at high temperatures its cellulose decomposes to volatile, flammable, organic compounds. The heat generated by burning decomposes more of the cellulose, propagating the flame. The suggestion of the researchers is that flameproofing compounds are members of a broad class of acidic compounds (which are electron acceptors, termed Lewis acids), that act as catalysts to direct the decomposition of the cellulose partly, but not completely, toward the production of water and carbon rather than flammable organic fragments. A certain amount of flammable gas is still produced, but at such a rate or in such composition that no burning takes place.

A second, subsidiary phenomenon is involved where organic resins are used. Some agents, when they ignite, leave a residue which renders the cellulose flameproof, while they themselves remain capable of burning because they contain a resin which is not susceptible to flameproofing by the catalytic dehydration reaction. To flameproof the agent, chemical groups can be introduced which react with its resinous portion to form products which reduce the flammability so that the mixture does not burn.

To summarize: The new theory proposes that universally in the flameproofing reaction the decomposition of cellulose is changed from a reaction giving volatile, flammable products to one giving mainly water and a highly carbonaceous char; and that the introduction of elements, such as bromine, into the flameproofing resins retards burning of these resins.

This basic knowledge should be helpful in research to modify the flameproofing resin in the direction of more efficient use or more economical production. It can be taken also as a criterion for selecting for further development only those organic resins which may be expected to have flameproofing properties for cellulose.

Fruits and Vegetables

New facts discovered concerning enzymatic breakdown of pectin

Pectic substances play an important role in the texture of certain fruits and vegetables during maturation, processing, and storage. They are also involved in the problem of keeping fruit juices clear and sparkling or orange juice appetizingly cloudy. A study of the action of enzymes which break down pectic substances was undertaken as the first step in a program of research to find the changes these substances undergo during softening, toughening, and deterioration of fruits.

Enzymic hydrolysis of pectic acid (which consists of long chains of chemically linked galacturonic acid residues) was traced by chemical analyses and paper chromatography. These studies showed that a somewhat random attack on the linkages between galacturonic acid units took place. Thus, mono-, di-, tri-, and tetragalacturonic acids rapidly appeared among the hydrolysis products. The mono-, di-, and trigalacturonic acids were separated from each other by paper chromatography on heavy filter paper and were crystallized as their brucine salts. These are the first crystalline derivatives of di- and trigalacturonic acids to be discovered, and offer a means of preparing these substances in pure form for further enzymic studies.

Another phase of this investigation deals with the characterization of naturally occurring pectic enzymes in fruits. Present results indicate that some of these enzymes are similar in their behavior to, and probably are identical with, those found in commercial enzyme preparations of fungal origin. This is an important finding since much of the backlog of information previously accumulated on properties of fungal enzymes can be utilized in development of methods for the prevention of undesirable textural changes in fruits.

New browning compound isolated from fruits

One of the important problems encountered in deciduous fruit processing is a discloration known as enzymatic browning. This discoloration occurs on the cut surface of fresh fruits and is particularly rapid and objectionable after thawing of frozen fruits. In addition to detracting from appearance and imparting an off-flavor, browning also reduces the nutritive value by destroying vitamin C. Special precautions required to retard browning during commercial processing operations frequently add significantly to cost of the processed product.

No wholly satisfactory methods of preventing this deterioration are known. Blanching (i. e., scalding) is effective but imparts a cooked flavor and is therefore not used for fruits frozen in piece form. Chemical treatments such as with ascorbic acid, hydrochloric acid, or sulfur dioxide, have other disadvantages which include high cost, loss of solids through leaching, limited effectiveness of treatment, or limitations imposed by public health considerations. Need for improved or more acceptable preventive methods is quite evident, but the attainment of this goal has been hindered by our limited understanding and knowledge of the chemistry of the browning process. Though it is known that browning occurs through the agency of a fruit enzyme (polyphenoloxidase) in the reaction between oxygen and derivatives of catechol called tannins, very little information has been available on the chemical identity of tannins in various fruits, the character-

istics of the enzyme, the chemical nature of the brown products, and the chemical steps that lead to browning. Investigations in progress at the Western Regional Research Laboratory are directed toward elucidation of these different phases of the general problem.

Of particular interest are recent developments in the isolation and identification of tannins, the browning substances in fruits. The task is difficult because these substances are present in very small amounts and must be separated from an exceedingly complex mixture of other chemical substances present in the fruit tissues. Separation has been accomplished through application of a multiple extraction method with the aid of a very efficient counter-current distribution apparatus. An examination of the tannins of several fruits with this powerful new tool has substantiated the presence of chlorogenic acid—also found in coffee—and led to isolation and identification of the hitherto undiscovered compound neochlorogenic acid. That these two substances are similar in chemical composition but differ in their structural configuration has been determined through X-ray diffraction, optical rotation, and spectrophotometric and chemical analyses.

The presence of these two related tannins has been shown in four varieties of peaches, in apricots, and in prunes. Though analytical studies are being continued, present results strongly suggest that these two substances are responsible for the major part of enzymatic browning. This knowledge will be helpful in devising means of interfering with and thus controlling the browning reaction.

This basic work also promises to be of help to fruit breeders developing hybrids of low browning susceptibility. If a correlation can be established between the tannin content of mature fruit and occurrence of the same or similar tannins in some tissue of fruit trees at the seedling stage, development of improved varieties would be greatly expedited. An even broader implication of this research is the contribution it may make to elucidation of the mysterious function of the enzymatic browning reaction in the life processes of fruits.

Compounds causing off-flavors in canned-stored grapefruit juice identified

The demand for citrus juices in our daily diet is based largely on their nutritive value, flavor, aroma, and color. Although abundant in fresh juices, these quality factors may be greatly altered when such juices are canned and stored.

In 1947 the California-Arizona Desert Grapefruit Industry Boards initiated a research program in cooperation with the Bureau's Fruit and Vegetable Chemistry Laboratory in Los Angeles, Calif., on the isolation and identification of the volatile flavoring constituents in fresh, canned, and canned-stored grapefruit juices. The purpose of this study was to determine the chemical changes in these juices leading to development of off-flavors and odors as a result of canning and storing. Later the project was transferred to the Laboratory's new location in Pasadena.

Because of numerous difficulties encountered in isolating unstable volatile compounds using ordinary vacuum-distillation methods, it was necessary to develop new chromatographic techniques. These new methods are not only useful for analysis of citrus oils, but should be applicable to analysis of other essential oils.

To study the chemistry of the flavor changes, volatile fractions from each of 2,500 gallons of fresh, canned, and canned-stored grapefruit juices were isolated under carefully controlled conditions, and separated into individual chemical compounds to determine changes which occur on heating and storing. Twenty-nine pure compounds and three groups of compounds (which could not be separated into individual components) were isolated and identified. These compounds could be conveniently grouped into three classes. Class I consisted of the volatile, water-soluble compounds. Although minor chemical changes were found as a result of heating and storing this class of compounds, it is unlikely that they were the cause of off-flavors.

Class II compounds consisted of essential oil hydrocarbons which made up the largest part of the volatile oil fraction. Although these compounds do not contribute materially to juice flavor, it was found that during the canning process or in subsequent storage they formed new compounds which caused off-flavors. Thus d-limonene was converted to alpha-terpineol and linalool monoxide, both of which produced off-flavors when small amounts were added to fresh grapefruit juice.

Class III compounds consisted of the volatile oil nonhydrocarbons. These compounds occur in relatively small amounts but contribute the largest part of the natural flavor. Changes found in these compounds were relatively minor.

It was also found that furfural, presumably derived from a breakdown of carbohydrates, was produced from heating and storing the canned juices. When added to fresh grapefruit juice, this material imparted a burnt flavor.

Oilseeds

New procedure developed for determining solid and liquid components of plastic fats

Plastic fats, such as margarine, butter, and shortening, are semirigid mixtures of solid and liquid components. The solid component, which may vary from 15 to 25 percent, imparts rigidity by enmeshing the liquid component. Control of hydrogenation of oils and formulation of spreads for specific plasticity requirements depend on control of the amount and properties of the solid phase. Hitherto, it has been necessary to employ indirect methods to analyze plastic fats for the amount of the two components. These methods depend upon determination of such physical properties as the change in volume or specific heat on melting of the solid component.

To provide a direct measure of the solid and oil phases, a new method has been developed at the Northern Regional Research Laboratory. The plastic fats are separated into the two components by an ultracentrifuge operating at 34,000 to 60,000 revolutions per minute (r. p. m.) and producing gravitational fields approximately 100 times greater than those attained in conventional laboratory centrifuges. Not only can the separate phases be analyzed for their amounts, but the composition, X-ray diffraction patterns, and other physical and chemical properties can be determined. This procedure has been applied to shortening, peanut butter, lard, butter, margarine, and global edible spreads.

The amount of solid phase obtained by ultracentrifugation of plastic spreads is greater than that found by the indirect methods of analysis previously used. Chemical analyses of the separated phases reveal the difference in degree of unsaturation of the solid and oil components. Solids from different types of plastic fats vary markedly in their unsaturation as measured by iodine value. Results obtained suggest that this centrifugation procedure may permit better evaluation of the role of chemical composition and the effect of crystal size and shape of the solid component in influencing rigidity of the solid-oil plastic fat systems.

Factors affecting stability of peanut oil determined

Rancidity has long been recognized as a troublesome factor in the marketing of roasted-peanut products, and scientific workers have observed marked differences in the stabilities of oil from raw peanuts and roasted-peanut products. An investigation of oil from 16 varieties of peanuts was made at the Southern Regional Research Laboratory to determine whether these differences could be attributed to fatty acid composition or to the presence of other constituents of the crude oils from these peanuts. A wide variation was found in linoleic acid content. Oils from Runner and Virginia peanuts contained the least linoleic acid and were the most stable, while oils from Spanish peanuts contained larger amounts and were the least stable. Content of linoleic acid, the most unstable acid in peanut oil, varied from 20 to 30 percent of the fatty acids in the oil.

This correlation between fatty acid composition and stability of peanut oils is in accord with results obtained in previous work showing that stabilities of refined oils hydrogenated (hardened) to various extents were inversely related to their contents of linoleic acid. Tocopherol components (naturally occurring materials which retard onset of rancidity) of the oils were not found to vary significantly in total tocopherol content or in the nature and distribution of individual components. These findings direct attention to the relationship between composition and stability of peanut oils and indicate a possible solution to the problem of extending the shelf life of roasted-peanut products.

New fundamental information on cottonseed, peanut, and tung oils

Complete information on the physical and chemical properties of vegetable oils and their constituent fatty acids is an ever-present need in research and in development and control of new processes to provide an increasing array of products. Fundamental research at the Southern Regional Research Laboratory has provided new and useful data on the properties of cottonseed, peanut, and tung oils and their constituent fatty acids.

New physical data on the solubility of cottonseed and peanut oils in solvents provide a fundamental basis for development of a practical solvent process that would increase the yield of salad oil. The data will also be useful in connection with the industrial application of solvent fractional crystallization to fats, oils, and oleaginous materials in general.

Information has been obtained on the influence of chilling temperature, chilling period, type of solvent, concentration, agitation, iodine value of the oil, degree of winterization (treatment for prevention

of gel under ordinary refrigeration) attained, proportion of solid glycerides separated, and ease of filtration. The results form the basis for two patent applications concerned with processes for the solvent winterization of cottonseed and peanut oils.

Data on the mutual solubility of ethyl and isopropyl alcohols and cottonseed oil have been obtained which will aid in the selection of optimum temperatures and moisture concentrations in the extraction of cottonseed oil with these solvents. In general, results indicate that isopropyl alcohol is the more desirable solvent since complete miscibility with the oil in all proportions can be attained at temperatures below its boiling point when it contains 10 percent or less by weight of water. Ethyl alcohol can tolerate only about 2 percent of water.

To determine the effect of isomerism (change in molecular structure) on thermal properties of the compounds, fundamental information was obtained on expansibility and other thermal properties of mono-unsaturated fatty acids. Positional and geometric isomers of the acids formed during hydrogenation have a profound influence on the physical properties of shortenings and margarines.

When linoleic acid—the major fatty acid in cottonseed oil—is hydrogenated, conjugated acids are formed and exist during some part of the process. The nature and amount of this conjugation was determined and fundamental information furnished for development of a rational theoretical approach to the hydrogenation process and to the formation of plastic fats.

Surface and interfacial tensions and other physical properties of fatty acids and their methyl and ethyl esters were determined for a wide range of fatty acids varying in chain lengths from 2 to 15 carbon atoms. Surface tension increased as length of the carbon chain increased, and the surface tension of ethyl esters was lower than those of the corresponding fatty acids. Similarly the viscosities of fatty acids and esters increased as the number of carbon atoms in the fatty acids chain increased. This basic information has been published and is used by industry in planning proper utilization of natural fats and oils and their derivatives.

Tung oil contains eleostearic acid—a fatty acid having a unique and versatile chemical structure. The present valuable use of tung oil in protective coatings depends upon the properties imparted by this acid. To extend the utilization of tung oil by developing new compounds which would have uses in fields other than protective coatings, it is important to know the structure of eleostearic acid. With the aid of infra-red analysis and binary freezing point, the structure of α- and β-eleostearic acid was determined, and it was shown that the two principal forms of this acid are stero-isomers. In the course of this research several new compounds of eleostearic acid were produced which have potential value in certain fields, particularly in that of plasticizers.

The applicability of n-octadecyl p-toluene sulfonate, a compound derivable from commercial vegetable oils, to a wide variety of reactions has been investigated by Tulane University under a research contract with the Bureau. A wide variety of compounds including phenols, alcohols, amines, salts, and aromatic compounds were alkylated. The products were all characterized and the yields obtained were frequently quite high. Results of this investigation have been

published and attention has been called to their ready availability. The characteristic structural groups present in many of the products and their availability will stimulate examination by manufacturers of lubricating oil additives, rubber chemicals, insecticides, plasticizers, surface active agents, etc.

Effect of environment and variety on composition of cottonseed investigated

The influence of environment and variety on the composition of cottonseed has been investigated by the Bureau's Southern Regional Research Laboratory in cooperation with the Bureau of Plant Industry, Soils, and Agricultural Engineering, to provide more complete basic knowledge of variables involved and factors contributing to variations in chemical composition. Two phases of the study have been completed.

Information on factors causing variations in the iodine value of cottonseed oils should aid industry in segregating oils for different purposes. Analysis of 312 samples of oil from 8 varieties grown during 3 years at 13 locations showed a variation in iodine value of from 88.1 to 116.8. This variation is attributed about equally to differences in the varieties of cotton and in the mean temperature prevailing during the maturation period when oil is elaborated in the seed. The iodine value varies inversely with mean temperature. Low mean temperatures contribute to production of oils of high iodine values. The influence of temperature is greater for some varieties studied than for others. Statistical relations for each of the 8 varieties included in the investigation have been developed from analytical and temperature data which should prove useful in locating areas from which cottonseed oils having high or low average iodine values may be obtained. High iodine value oils are desired generally for production of winterized salad oils from cottonseed, as yields obtained are higher and processing costs lower.

Information on the types and amounts of phosphorus compounds in cottonseed kernels is basic to any comprehensive consideration of the nutritive value of cottonseed meals. An analytical system for determination of phosphorous compounds in plant materials has been devised and used for analysis of 58 samples of cottonseed representing 8 varieties of cotton grown at 13 locations during 3 years. These samples were analyzed for total, acid soluble, phosphatide, inorganic, phytin, nucleic, and carbohydrate phosphorus. Variations in results are attributed almost entirely to environmental factors. Of particular significance is the observation that phytin phosphorus, a type having doubtful nutritive value, represents approximately three-fourths of the total phosphorus in cottonseed kernels.

Poultry, Dairy, and Animal Products

New uses for pure caseins

Ordinary casein produced from skim milk by acidification is an important commercial protein used in coatings, adhesives, and fibers. Although casein had been considered a pure protein, recent analysis has shown it to be composed of three protein components designated α-, β-, and γ-casein. Proportions of each are: 75, 22, and 3 percent, respectively. A practical method has been developed at the Eastern

Regional Research Laboratory for separation of the components. In principle, the method consists of fractional precipitation by adding water to a solution of casein dissolved in a concentrated urea solution.

The separated casein components differ in composition and properties. Bristle fibers made from pure β-casein are superior to fibers from α-casein or unfractionated casein. Highly stretched β-casein fibers have a dry tensile strength of 24,000 pounds per square inch, 20 percent higher than a comparable value of α-casein. The high value of 14,000 pounds per square inch for the wet strength of stretched β-casein fiber is of particular importance since a value of 4,000 pounds per square inch for the wet strength of ordinary casein fiber limits its use in water. The X-ray diffraction pattern of the stretched β-casein fiber shows a higher degree of orientation than the α-casein fiber and is consistent with its greater strength.

Important new biochemical results have been obtained by the use of pure casein components furnished to investigators in other laboratories. At the Rockefeller Institute it was reported that phosphates of the prostate does not split off the phosphorus of ordinary casein or β-casein, but splits phosphorus rapidly from α-casein. It was further shown that addition of β-casein to α-casein prevented the action of this phosphatase on α-casein. Studies at the New York University College of Medicine have shown that splitting of β-casein by the proteolytic enzyme trypsin is markedly different from the splitting of α-casein. The insoluble hydrolytic substance produced when trypsin acts on β-casein for a short time was used to demonstrate the asymmetry of the structure of β-casein. Similar studies at the University of Illinois shaw that proteolytic enzymes produced by micro-organisms hydrolyze β-casein in a unique manner.

New research tool for biochemical investigations of lipid changes in body fluids and tissues

A new micromethod developed by scientists at the Eastern Regional Research Laboratory makes possible the determination of changes in fatty acid composition of lipids in body fluids—such as blood and lymph—and in tissues, without sacrifice of the experimental animals. The method is also suitable for the study of lipid changes in living plants. Only 1 to 2 milligrams of lipid are required for determination of the polyunsaturated fatty acid components although the method gives equally good results on larger quantities up to 80 milligrams.

This development is a byproduct of a fundamental investigation on the mechanism of the isomerization produced by the action of strong alkali at high temperatures on pure unsaturated fatty components. Optimum conditions were found for making the unsaturated components absorb strongly in the ultra-violet spectral region. This absorption is measured spectrophotometrically and is the basis for the sensitive micromethod.

The method should be invaluable in medical research on lipid changes in different tissues resulting from pathological conditions such as are produced by disease, atomic and X-ray irradiation, and abnormal diets.

New method of separating fatty acids

Many investigations on fats, such as oxidation, polymerization, and nutrition studies, require large quantities of pure unsaturated fatty

acids having the same configuration as that in the fat from which they are derived. Previously known procedures consisted in solvent recrystallization of mixtures of fatty acids at temperatures from −50° to −90° C., recrystalization of mixed fatty acid soaps, and more recently, chromatographic separation. Although large quantities of pure acids can be obtained by the first two procedures, they are time-consuming and require large quantities of organic solvents. The last procedure is adaptable at present to the preparation of only small quantities, although the purity is high.

Research at the Eastern Regional Research Laboratory has shown that purified oleic, linoleic and linolenic acids (or their methyl esters) can be prepared in good yield from suitable fats. The procedure involves selective precipitation of the desired acid (or ester) from a methanol solution of the mixed acids of a fat by formation of an insoluble urea complex. The main advantages of such a procedure are: (1) All operations are conducted at or above 0° C. and usually at room temperature; (2) large-scale separations can be conveniently carried out; (3) reagents are cheap, plentiful, and readily recovered; (4) yields are good and purity is satisfactory for most purposes (90–99 percent); (5) configuration of the acids (or esters) is unaltered, and (6) no specialized apparatus is required. It is now possible to obtain purified linoleic and linolenic acids in almost any laboratory quantity without difficulty.

Structure study of the egg protein lysozyme

One of the major unsolved problems of biology is the detailed structure of a corpuscular protein. The remarkable chemical specificity shown by many proteins must be due in part, at least, to the geometrical arrangement of certain amino acids. Knowledge of this arrangement is necessary for a complete understanding of the reactivity of proteins and could conceivably lead to control of innumerable biological reactions which are of importance in the utilization of agricultural materials.

Lysozyme, obtained from egg white, is a particularly promising protein for study because it is both a bactericide and an enzyme, has a comparatively low molecular weight, and can be readily crystallized as the chloride salt.

The Western Regional Research Laboratory has been making a collaborative investigation with the California Institute of Technology on the structure of air-dried lysozyme chloride crystals. Complete 5-degree oscillation photographs have been taken around two axes of the tetragonal crystal, and from these data the symmetry and unit cell size have been calculated. By flotation in a xylene-ethylene bromide mixture the density of the crystals was determined to be 1.305 gm./cm^3. Using this value, together with the X-ray data, the molecular weight of lysozyme chloride was calculated to be 13,900±600.

Over 600 reflections have been recorded for the lysozyme chloride crystal. These reflections have been indexed and their relative intensities estimated by the multiple film technique. The data thus obtained have been used to calculate a complete three-dimensional Patterson diagram by means of automatic computing machines at the California Institute of Technology. Interpretation of the Patterson diagram has led to a determination of the probable arrangement of the

lysozyme molecules in the unit cell. It has also been possible to derive distributions of scattering matter in the molecule which are compatible with the principle features of the diagram.

No detailed information about the structure of the lysozyme molecule could be obtained from this investigation because the smallest spacing recorded from the air-dried crystals is too large to permit resolutions of the order of interatomic distances. The information obtained, however, appears so promising that the collaborative arrangement with the California Insitute of Technology is being continued in order to investigate the much more extensive X-ray data given by lysozyme chloride crystals when immersed in their mother liquor. Because reflections from wet crystals extend to much larger angles, interpretation of these data holds promise of furnishing more detailed information concerning the configuration of protein chains and geometrical arrangement of heavier atoms.

Sugars and Special Plants

Determination of rate of crystallization of amorphous sucrose

Certain dehydrated food products—for example, spray-dried fruit juices—exhibit undesirable changes in properties upon exposure to air of normal humidity, becoming gummy and finally grainy in texture. The gumminess has been recognized as a consequence of moisture absorption by the amorphous solid sugars which result from rapid drying; the grainy texture results from the eventual crystallization of sugar from the moistened amorphous solid. Recent investigations at the Western Regional Research Laboratory have thrown new light on the mechanism of these changes and have secured information about the rates at which they occur.

The behavior of amorphous sucrose in atmospheres of 30 percent or higher humidity differs markedly from its behavior at humidities of 25 percent or less. At the low humidities samples absorb moisture from the atmosphere up to an equilibrium value and then remain constant in weight; they show no evidence of crystallization during a period of many months. At 30 percent humidity, on the other hand, an initial gain in weight is succeeded by a short period of equilibrium and then a gradually accelerating decrease in weight, accompanied by crystallization. During the period of initial gain, a highly viscous solution is formed, and the powder shows a marked tendency to cake. In about 10 days a crystalline crust has formed around each particle and the powder is once again free-flowing. Crystallization then proceeds more rapidly; it is complete by the end of the 14th day. Even a slight rise in relative humidity accelerates these changes markedly. At 32 percent, crystallization is complete in 4 days; at 35 percent, in less than 1 day.

The time required for complete crystallization is about halved if the sample of amorphous sucrose is seeded with a small amount of finely ground crystalline sucrose. On the other hand, even a little pectin added to the sample slows the rate of crystallization markedly. The complex mixtures of substances formed when natural products are dried would doubtless persist longer in the amorphous condition than would a pure compound like sucrose.

Techniques of measurement developed during this investigation will facilitate applied studies aimed either at preventing or at inducing

the transformation of amorphous to crystalline condition in various dry food products.

Studies of objectionable floc in certain beet sugars

Sugar is one of the purest man-produced organic substances; nevertheless, when certain lots of beet sugar are made into bottlers', pharmaceutical, or soda fountain sirups, an objectionable flocculant precipitate appears, causing loss in consumer acceptance. A similar floc sometimes occurs in cane sugar. Although the actual amount of material making up the floc is small, it is so light that it appears to be present in considerable bulk. The importance of the problem to the sugar industry is emphasized by the fact that the bottling trade furnishes the largest industrial market for sugar.

Research on this problem requires isolation and identification of substances present to the extent of only a few parts per million. The Western Regional Research Laboratory has separated the floc into four fractions. The major fraction appears to be similar to the fat occasionally used to break foams which form in the evaporators and vacuum pans. The second important fraction has been identified as saponin, thus confirming in part a finding recently made at one of the major beet sugar plants. The third fraction is similar to the first, and the fourth is insoluble material containing a large proportion of silica.

Apparently the fats and other insoluble materials adhere to the saponin, and this mixture forms the floc in acidified sugar sirup. By application of paper electrophoresis techniques, the presence of two saponins has been shown. Although the number of experiments is limited, it appears that the amount of one of these saponins (the faster one in the electric field) decreases as the sugar goes through regular processing steps in the factory, and is of lesser importance in floc formation. The other saponin, which seems to be more implicated in floc formation, is now under investigation to establish its composition. Studies are also under way on a rapid quantitative analytical method that can be used in the factory to determine the concentration of saponin in processing juices.

Saponin is noted as a foaming agent, and this property gives rise to trouble in the operation of evaporators and vacuum pans. Industry now spends many thousands of dollars to control foaming. Consequently, research devoted to development of new methods of saponin removal may not only increase the quality of a widely used food, but also reduce the cost of factory operations.

New data on minor constituents of sugarcane aid to processing

Significant progress has been made concerning organic acids and starch—nonsugar substances—in sugarcane. Although present in relatively small amounts, they affect processing of juice and recovery of sugar to a remarkable degree. The initial step in investigations at the Southern Regional Research Laboratory, was to develop a method of preserving sample material for subsequent analysis. This problem was solved by quickly freezing the fresh raw juice and drying it by subliming the ice under high vacuum. With well-preserved sample material available for investigation, it was possible to apply precise and specific laboratory methods such as chromatography for the quan-

titative separation and identification of substances not previously reported in sugarcane.

In the investigations the occurence of both mesaconic and fumaric acids was established for the first time. Published reports of the presence of succinic and citric acids had not been supported by adequate identifications of these compounds, but both have now been isolated by chromatographic methods and identified positively by standard procedures. Reliable evidence for the presence of glycolic acid was obtained for the first time and the occurrence of malic and oxalic acids confirmed. At least one more hitherto unreported organic acid has been isolated and work is in progress on its identification.

Quantitative data have been obtained on the starch contents of different varieties of cane by a specific and sensitive method suitable for determination in low concentration. Generally assumed to the contrary, investigations established that some starch is found in all varieties of cane currently used or being developed for commercial introduction in Louisiana. In most cases the concentrations in cane and raw juice are low, but they reach significant proportions during evaporation. A finding of importance is that the starch in sirups is strongly adsorbed by growing sugar crystals, and that raw sugars invariably contain amounts of starch sufficient to account for some of the difficulties in their refining. This minor constituent may thus prove to be a limiting factor in yield of raw sugar as well as a major cause of variations in refining and quality of refined sugars. Data accumulated on starch content will serve as a basis for selecting new varieties in which this constituent does not reach objectionable proportions, as well as for developing means of eliminating excessive amounts of starch in juices to be processed.

These studies of the composition of cane are being extended to pectic materials and compounds containing nitrogen and phosphorus. When completed, the results should provide needed information on relation of processing quality to composition. This will permit selection of canes of the best processing quality on the basis of laboratory analyses that can be carried out in the early stages of the breeding process. Investigations of the composition of canes are being performed in connection with the evaluation for commercial processing of new varieties developed by the Bureau of Plant Industry, Soils, and Agricultural Engineering. Milling and pilot-scale processing experiments in the evaluation studies are carried out in cooperation with Louisiana State University.

Advances in fundamental research on pine gum products

New and profitable outlets are urgently needed to stimulate the demand for gum turpentine and gum rosin and to increase the economic value of the pine gum crop. The Bureau's Naval Stores Station is giving increased attention to basic investigations designed to achieve this objective.

Application of chromatographic and optical methods of analysis to gum rosin and derived products has revealed the presence of two heretofore unrecognized acids. In further research, sufficient quantities of these acids will be isolated to permit a determination of their properties and reactions. Results of this work are expected to help clarify the mechanism of isomerization and disproportionation of

rosin, and could lead to the development of new and improved rosin products.

Industrially useful acids have been produced experimentally by oxidation of alpha pinene, a component of turpentine, but the methods employed were not economically feasible for commercial use. Progress is being made in further work to develop a practical process and to evaluate potential uses for the acids produced. The research is in progress at the Naval Stores Station and under Bureau contracts with the Armour Research Foundation and the Georgia Institute of Technology.

Pinic acid, and the related acid pinonic, have been produced on a pilot-plant scale to provide samples for evaluation purposes. In cooperative work with the Rohm & Haas Co. certain esters of pinic acid have been found to be excellent plasticizers for polyvinyl chloride resins, better in some respects than dioctylphthalate, the most widely used plasticizer for this type of resin.

The fiber- and film-forming properties of pinic acid polymers are under study in a cooperative investigation with the American Viscose Corporation. As anticipated from the unsymmetrical nature of the pinic acid molecule, polymers made from it were unsuitable for manufacture of synthetic fibers for general textile use. In plastic composition, however, the polymers had desirable properties, meriting further study.

General

Infrared spectrophotometry aids research

Organic molecules absorb infrared radiation at frequencies that are strongly characteristic of their structure and composition. When the molecules are complex the infrared spectrum is particularly useful in identification, mixture analysis, and structure determination. Two applications of infrared spectrophotometry being made at the Eastern Regional Laboratory are cited in illustration.

Infrared Spectrophotometric Determination of Trans Fatty Compounds.—Although it had been recognized that trans fatty compounds have a profound effect on the physical properties of processed fats, notably hydrogenated shortenings, no method for their precise and accurate analysis was available. Furthermore, it was suspected that in other important areas of investigation in fat chemistry, such as autoxidation, isomerization, dehydration, and polymerization, trans compounds were probably formed and exerting a notable influence on the reactions and properties of resulting products.

The observation that trans monounsaturated fatty compounds showed a characteristic infrared absorption band at a wavelength of about 10.4 microns, was the basis for development of an infrared spectrophotometric analytical method for determination of trans fatty compounds. A large number of pure model trans acids, esters and alcohols, as well as the corresponding cis and saturated compounds were prepared and the infrared absorption characteristics of these compounds and selected mixtures of them determined. From this fundamental information, a rapid, precise and accurate analytical method was developed which is now being used almost universally in work on fats.

Application to Steroid Research.—In screening several thousand plant samples for steroidal sapogenins possibly useful as starting materials for the synthesis of cortisone, it was necessary to find analytical methods which could be carried out rapidly. Infrared methods met the requirements admirably for the spectra of the sapogenins were found to be distinctively different from one another. In addition to distinguishing individual sapogenins the infrared spectrum is also used to identify the steroidal sapogenius as a class, since it was found that a particular group of four absorption bands occur in the spectra of all sapogenins. Furthermore, two of these bands indicate by their relative intensity whether the sapogenin molecule has the "normal" or "iso" configuration, and one band is sufficiently constant in intensity for all sapogenins to permit its use in assaying a mixed sample for total amount of sapogenin. Neither of these type classification determinations can be made by ordinary chemical methods.

In following the side-chain transformations by which sapogenins are converted to pregnane derivatives, infrared spectra have been used in determining the rates of reactions and the structure of intermediate compounds produced. Infrared spectra helped demonstrate also that structures for steroidal saponins proposed in the literature are incorrect and that the steroid component in saponins is not changed in structure on isolation.

New amino acids discovered in antibiotics

Although many antibiotics, like proteins, are largely composed of amino acids, significant differences are beginning to appear, particularly in the molecular structure of certain of the amino acids. Two unusual sulfur-containing amino acids have been found by the Western Regional Research Laboratory in acid hydrolysates of subtilin. Together they account for the sulfur content of subtilin to the exclusion of the common sulfur-containing amino acids—cystine and methionine.

One of these sulfide amino acids (empirical formula $C_7H_{14}O_4N_2S$) makes up 25 percent of the weight of subtilin. From it L-alanine and D-alpha aminobutyric acid are obtained by removal of sulphur, and further study has shown that the new acid must be one of two of the eight possible forms of β-methyl-lanthionine. Although its discovery in subtilin represents the first knowledge of this new amino acid, it has since been found in the antibiotic nisin by investigators at the University of Oxford, England, and its presence in the antibiotic cinnamycin is suggested by investigators at the Northern Regional Research Laboratory. The three types of bacteria that produce these three antibiotics are not at all closely related.

The second amino acid discovered in subtilin is the closely-related mesolanthionine ($C_6H_{12}O_4N_2S$). This compound was first discovered about 12 years ago by scientists in the (then) Bureau of Agricultural Chemistry and Engineering; it was formed from the common amino acid cystine when proteins containing the latter were treated with alkali. It has also been discovered recently in nisin. In subtilin and nisin it appears for the first time as a normal constituent of the active, undegraded peptides.

These new amino acids could be formed by condensation of the common amino acid cysteine and uncommon forms (optical isomers)

of threonine and serine in a reaction similar to that between the analogous amino acids homocysteine and serine in the liver as well as in micro-organisms. Discovery of the new amino acids will encourage a search for reactions, involving these or similar compounds, which will be of significance in the sulfur metabolism of animals, plants, and micro-organisms. In addition, their structures suggest ways in which antibiotics may act, such as: (1) By interfering in normal formation of proteins from amino acids, or (2) by interfering in normal functioning of vitamins or co-enzymes which contain amino acids.

Discovery of a new amino acid anywhere in nature makes it likely that it will be found elsewhere in biological material—in low concentrations, perhaps, but possibly playing an important role, such as by conferring activity on an enzyme or by acting as a transition compound in other biochemical processes.

Zymonic acid—a new chemical from yeast

Extensive work on molds and bacteria has demonstrated their remarkable capacity for producing new and useful chemicals such as alcohols, acids, carbohydrates, antibiotics, etc. The abilities of yeasts in this respect, however, have received little consideration with the exception of alcohol fermentation. As part of its search for new products, the Northern Regional Research Laboratory has examined 120 species of yeasts from 24 genera. From about a dozen species which produced acids in 25 to 50 percent yield, one yeast, *Trichosporon capitatum*, was selected for detailed study.

As its main product this organism was found to produce an unstable acid which could be isolated in the form of its stable methyl ester. Structural studies have established with reasonable certainty that the acid, as it appears in the culture liquor, is an equilibrium mixture of 3,5-diketo-4-methyl-tetrahydrofuroic acid and its enol form.

Further studies showed that the same methyl ester could be isolated from culture liquors of *Hansenula subpelliculosa* and *Kloeckera brevis*, two yeasts quite unrelated to one another or to *Trichosporon capitatum*. Such widespread distribution of the acid, which was designated as "zymonic acid," suggested strongly that it might be a part of a hitherto unsuspected pathway used by micro-organisms in the breakdown of glucose. To facilitate a more extensive survey of the yeasts, it was found that the laborious isolation of the methyl ester could be circumvented by direct conversion of zymonic acid into easily isolated crystalline azo derivatives. By use of this method it was possible to show that zymonic acid is also produced by the yeasts, *Pseudomonilia rubicundula*, *Torulopsis laurentii*, *Debaryomyces guilliermondii*, *Nematospora coryli*, and *Torula mellis*. It was not found in culture liquors from the yeasts, *Brettanomyces lambicus*, *Hansenula saturnus* and three different strains of *Saccharomyces cerevisiae*.

Much of our present knowledge of the metabolism of higher plants and animals has issued from fundamental studies of the behavior of micro-organisms. Discovery of a new metabolic product such as zymonic acid is, therefore, of interest, particularly since it is a beta-keto acid and hence may occupy a key position in a new pathway analogous to that ascribed to oxalsuccinic acid in the Kreb's tricarboxylic acid cycle.

Studies on gibberellin—a plant growth regulator

A common plant disease in Japan, known as Bakanae-byo, is caused by the fungus *Gibberella fujikuroi* (*Fusarium moniliforme*). It occurs mainly in rice nurseries, and the seedlings attacked differ from normal seedlings in that they grow to abnormal length, have more slender leaves, and stems of paler green. In 1926, culture filtrates of the "Bakanae" fungus were shown to produce these characteristic symptoms in the same manner as the fungus itself. In 1939, the isolation of a very potent growth stimulating compound (gibberellin A) from *F. monilforme* culture liquors was reported. Since then 21 more papers have appeared from Japan on the chemistry and phytopathology of gibberellin.

In recent years an extensive investigation of the action of organic compounds on plant growth was undertaken by American investigators, and in pursuance of this work gibberellin concentrates were preserved. The Japanese work was confirmed and results were judged to be important enough to warrant further study. It was felt that a satisfactory method for the production of gibberellin should be worked out in this country and published in English in easily available journals so that this unique compound would be more generally available for investigation.

A reliable assay method using rice seedlings was developed by the Northern Regional Research Laboratory and studies were undertaken to find cultural conditions that would produce gibberellin with the Japanese organism and medium. It was found impossible to produce the compound by this means. However, it was possible to obtain gibberellin activity in culture liquors from an American strain of *F. moniliforme*. A simple method for the isolation of crystalline gibberellin from the culture liquor was developed and about 30 grams of crude gibberellin were accumulated.

Chromatographic methods were investigated as a means of resolving crude gibberellin into its components. Phosphate buffer on celite was found effective. The mixture was separated into the Japanese gibberellin A (optical rotation +35°) and a new gibberellin, designated as X, with a rotation of +88°. Both showed the same potency in rice-seedling tests.

Analytical data on gibberellin X show it to be a $C_{19}H_{24}O_6$ monobasic acid. Its chemical relationship to gibberellin A, purported to be a $C_{22}H_{26}O_7$ compound, is under investigation.

American investigators now have the means whereby they can obtain the pure gibberellins for study. These are unusual compounds and merit further investigation because of their unique ability to increase markedly the number of plant cells without affecting their size and shape.

FUNCTIONAL ORGANIZATION OF THE BUREAU

The Bureau of Agricultural and Industrial Chemistry is organized on a decentralized basis. Its research is conducted at four large regional research laboratories—located at Wyndmoor, Pa., Peoria, Ill., New Orleans, La., and Albany, Calif.—and at several smaller specialized branch stations. The Chief of the Bureau and his immediate staff, including five Assistant Chiefs, are located in Washington, D. C.

The Assistant Chiefs are assigned responsibility for particular phases of the Bureau's activities. There are four Regional Directors, each of whom is responsible to the Chief of the Bureau for all research in his region. The organization of the Bureau is as follows:

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